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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part III. The System: $Pb(NO_3)_2$-NH_4NO_3-H_2O

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Received September 5, 1947

(Communicated by Dr. K. S. Gururaja Doss, F.A.SC.)

The difference in the behaviour of potassium nitrate and sodium nitrate in the formation of complex compounds with lead nitrate, as seen in the earlier parts of this series, led us to study the system: $Pb(NO_3)_2$–NH_4NO_3–H_2O.

G. Malquori,[1] from measurements of conductance and viscosity of solutions of lead nitrate, of ammonium nitrate, and of mixtures of these two salts at temperatures between 15° C.–60° C., adduced evidence for the existence of a complex of the type:—$2\,NH_4NO_3.Pb(NO_3)_2$.

Later, W. M. Madgin and K. Laybourn[2] and Arthur E. Hill and Nathan Kaplan[3] studied the above system in the absence of water and found no evidence for the double salt in the solid state. Thus only one compound was known or suspected in aqueous solution and none in the solid state. But our experiments with potassium nitrate led us to expect three compounds corresponding to the potassium salt. The physico-chemical properties investigated are density, viscosity, specific conductivity and surface tension. From viscosity and surface tension, rheochor and parachor values were also calculated.

Experimental

For the preparation of solutions and determination of density, viscosity and conductivity similar procedure was adopted as explained in Part I. Surface tension values were obtained by the "drop method" using the Traube stalagmometer. Great care was exercised to ensure that the dropping surface was perfectly free from greasiness. After each experiment it was carefully cleaned by chromic acid mixture, and polished when necessary by means of a piece of fine soft linen or clean cotton-wool, as even slight traces of grease (invisible) on the dropping surface markedly altered the size of the drops. Care was taken to preserve the apparatus from being shaken by the stirring part of the thermostat. The velocity of flow of liquid

in the stalagmometer was regulated by attaching a fine capillary to the upper part of the tube.

Surface tension was calculated by using the formula:—

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2}$$

(γ_1 and γ_2 are the surface tensions of the two liquids; and n_1 and n_2 are the respective numbers of drops given by the same volume of the liquids, the densities of which are d_1 and d_2 respectively). Water was taken as the standard liquid with $\gamma = 70{\cdot}7$ dynes/cm. at 35° C.

The solutions had the following composition:—

Solution Numbers	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
C.C. Pb $(NO_3)_2$ added to 20 c.c. NH_4NO_3 soln.	0 c.c.	2	3	4	5	6	7	8	9	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40c c.

Observations and Discussion

The values of viscosity, rheochor and conductivity are given in the following tables:—

TABLE I

Specific Conductivity

Cell constant : 24·25 Temperature : 30 ± 0·05° C.

Soln. No.	Sp. Cond. × 10^{-2}	Resist.*	Soln. No.	Sp. Cond. × 10^{-2}	Resist.*
1	4·4840	541	14	7·5750	320
2	4·8770	497	15	8·0525	301
3	5·0710	478	16	8·2170	295
4	5·2915	458	17	8·4112	288
5	5·5748	434	18	8·6561	280
6	5·6745	427	19	8·9106	272
7	5·8272	416	20	9·1380	265
8	6·0600	400	21	9·3930	258
9	6·3145	384	22	9·6160	252
10	6·5860	368	23	9·8535	246
11	6·7140	361	24	10·098	240
12	6·9080	351	25	10·304	235
13	7·2120	337			

* Resistance refers to the value when the null point is at the centre of the bridge.

TABLE II

Viscosity

Temperature : 30 ± 0·05° C.

Soln. No.	Density	Viscosity*	Soln. No.	Density	Viscosity
1	1·0090	0·8981	14	1·0926	0·9606
2	1·0183	0·9055	15	1·1019	0·9662
3	1·0229	0·9079	16	1·1112	0·9803
4	1·0276	0·9103	17	1·1205	0·9870
5	1·0322	0·9127	18	1·1298	0·9955
6	1·0369	0·9186	19	1·1393	1·0030
7	1·0415	0·9218	20	1·1484	1·0106
8	1·0462	0·9242	21	1·1577	1·0180
9	1·0508	0·9265	22	1·1670	1·0260
10	1·0554	0·9279	23	1·1763	1·0337
11	1·0647	0·9388	24	1·1856	1·0414
12	1·0740	0·9461	25	1·1949	1·0485
13	1·0833	0·9534			

* Viscosity values are relative, *i.e.* (H_2O : 1).

The values in the two tables are represented graphically in Figs. 1 and 2. It will be noted that the curves indicate three breaks corresponding to 5 c.c., 10 c.c. and 20 c.c. of lead nitrate. The molecular ratios between ammonium nitrate and lead nitrate at these points correspond to the compounds :—

$4\,NH_4NO_3.Pb(NO_3)_2$, $2\,NH_4NO_3.Pb(NO_3)_2$ and $NH_4NO_3.Pb(NO_3)_2$

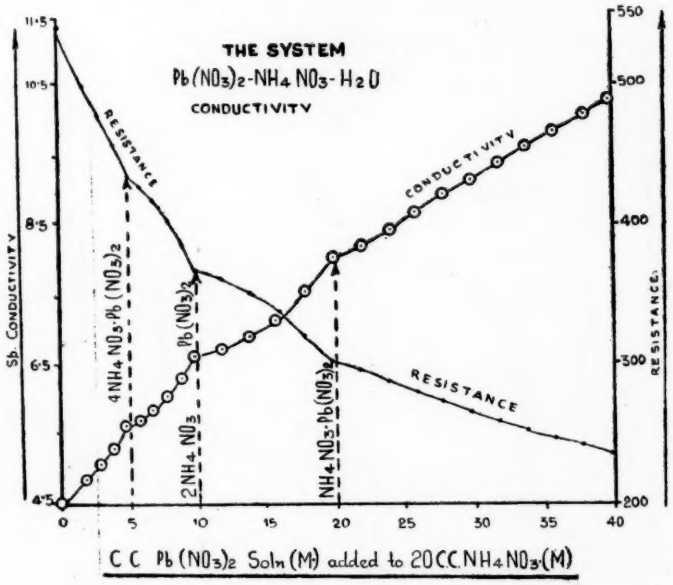

FIG. 1

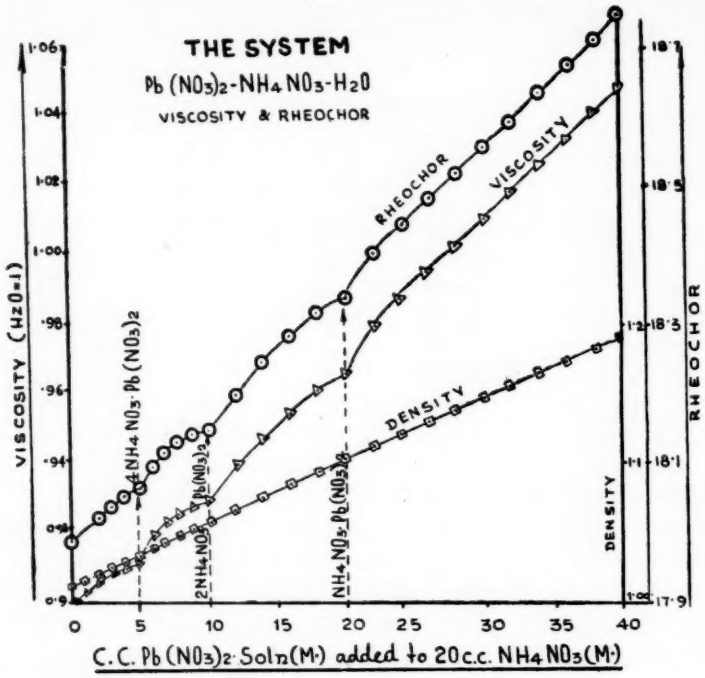
THE SYSTEM
Pb (NO3)2-NH4 NO3-H2O
VISCOSITY & RHEOCHOR
VISCOSITY (H2O=1)
RHEOCHOR
DENSITY
4NH4 NO3·Pb (NO3)2
2NH4 NO3·Pb(NO3)2
NH4 NO3·Pb(NO3)2
C.C. Pb (NO3)2 Soln(M) added to 20c.c. NH4 NO3(M)

FIG. 2

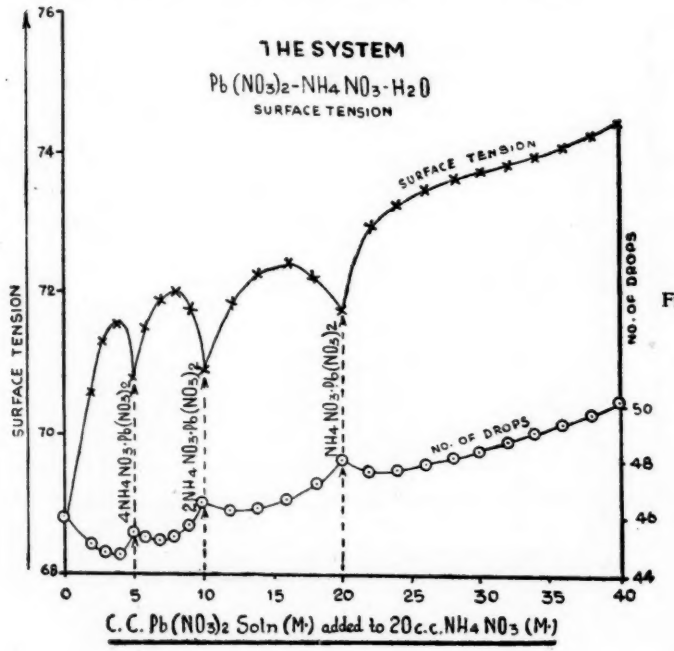
THE SYSTEM
Pb (NO3)2-NH4 NO3-H2O
SURFACE TENSION
SURFACE TENSION
NO. OF DROPS
4NH4 NO3·Pb(NO3)2
2NH4 NO3·Pb(NO3)2
NH4 NO3·Pb(NO3)2
C.C. Pb (NO3)2 Soln (M) added to 20c.c. NH4 NO3 (M)

FIG. 3

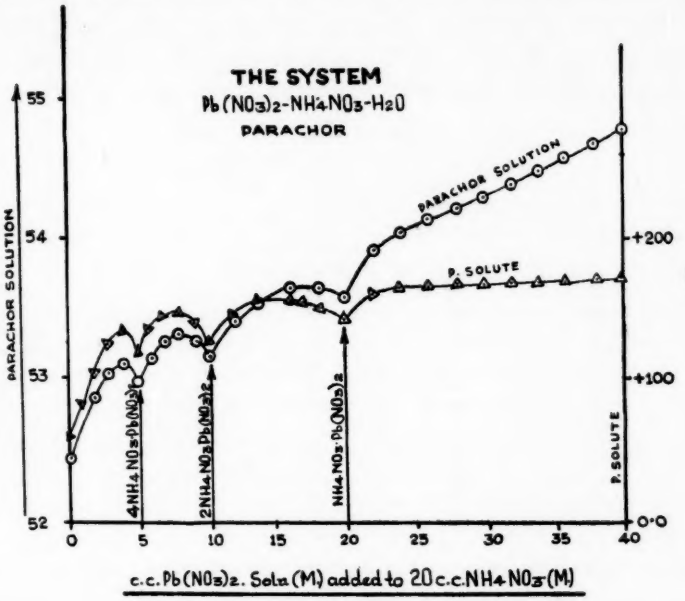
THE SYSTEM
Pb(NO3)2-NH4NO3-H2O
PARACHOR
PARACHOR SOLUTION
P. SOLUTE
4NH4NO3·Pb(NO3)2
2NH4NO3·Pb(NO3)2
NH4NO3·Pb(NO3)2
c.c. Pb(NO3)2. Soln (M) added to 20 c.c. NH4NO3 (M)

FIG. 4

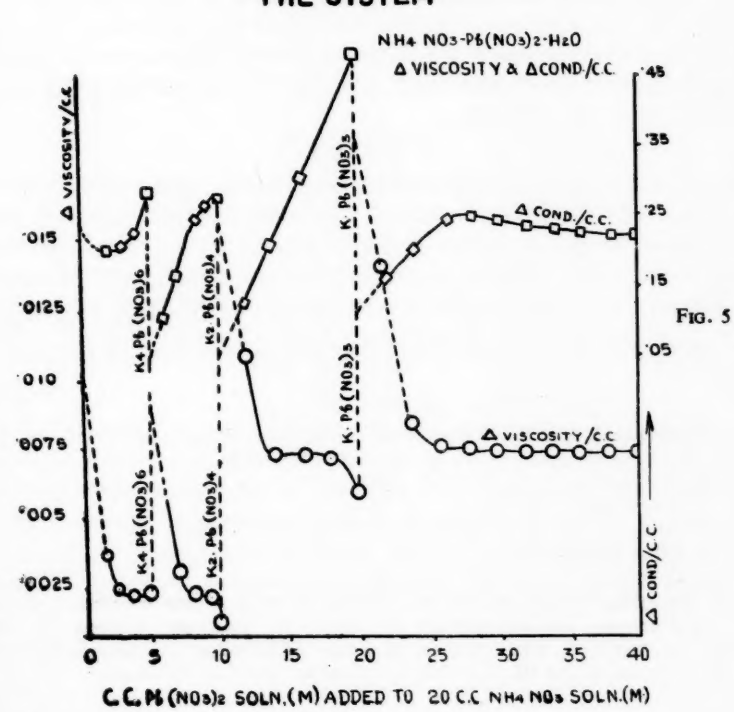
THE SYSTEM
NH4NO3-Pb(NO3)2-H2O
Δ VISCOSITY & Δ COND./C.C.
Δ VISCOSITY/C.C.
Δ COND./C.C.
K4Pb(NO3)6
K2Pb(NO3)4
K1Pb(NO3)3
C.C. Pb(NO3)2 SOLN.(M) ADDED TO 20 C.C NH4NO3 SOLN.(M)

FIG. 5

The following table shows the values of surface tension and Parachor (Solution).* When these values are plotted (Figs. 3 and 4), they yield exactly similar curves as with other properties.

TABLE III

Surface Tension and Parachor

Temperature : 35 ± 0·05°C.

Soln. No.	Surface tension	Parachor Solution	Soln. No.	Surface tension	Parachor solution
1	68·38	52·43	14	72·11	53·64
2	70·55	52·86	15	71·61	53·59
3	71·28	53·01	16	73·00	53·92
4	71·60	53·11	17	73·25	54·04
5	70·75	52·98	18	73·50	54·14
6	71·47	53·15	19	73·62	54·20
7	71·93	53·26	20	73·75	54·30
8	72·11	53·32	21	73·85	54·40
9	71·75	53·27	22	74·00	54·50
10	70·80	53·14	23	74·15	54·59
11	71·85	53·40	24	74·30	54·68
12	72·30	53·52	25	74·45	54·75
13	72·43	53·64			

Attention may be drawn to " Curve Number of Drops " in Fig. 3, where the graph refers to the number of drops of the liquid formed in the stalagmometer corresponding to different concentrations. It may be noticed that the drop count without any further calculation gives a curve analogous to those obtained with properties deduced as a result of elaborate calculations. Fig. 5 represents the " differential variation " curves which bring out the transition points even better.

CONCLUSION

The results obtained with ammonium nitrate are unlike those of sodium nitrate, but very much like those of potassium nitrate. The three breaks in the curves at concentrations corresponding to 5 c.c., 10 c.c. and 20 c.c. of lead nitrate, seem to indicate the presence of three complexes of formulæ:—

$4\,NH_4NO_3.Pb(NO_3)_2$, $2\,NH_4NO_3.Pb(NO_3)_2$ and $NH_4NO_3.Pb(NO_3)_2$,

exactly analogous to the potassium compounds as described in Part I of this series.

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3. Arthur E. Hill and Nathan Kaplan .. *J. Am. C. S.*, 1936, 1644–45.

* The limitations of Rheochor and Parachor for the study of the constitution of molecules are well known. They are however, very uscful for diagnostic purposes, for which only they are employed here. The actual values of Rheochor and Parachor (Solute) are omitted from Tables II and III., but their variations are shown in the Graphs.

FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part IV. E.M.F. Measurements

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Received September 5, 1947

(Communicated by Dr. K. S. Gururaja Doss, F.A.SC.)

ACCORDING to Lewis and others,[1] the addition of either sodium or potassium nitrate to a solution of lead nitrate causes a considerable diminution of the plumbous ion concentration, thus indicating complex formation in each case, although to a greater extent with the potassium salt.

The method adopted by us (*cf.* Parts I to III) enables us to determine not merely the number of complex compounds produced but also to read off from the graph their exact formulæ. Viscosity, surface tension, conductivity, F. point and related properties indicated the possible existence of three definite compounds in each of the systems: KNO_3–$Pb(NO_3)_2$–H_2O and NH_4NO_3–$Pb(NO_3)_2$–H_2O. We have now sought to obtain additional evidence from E.M.F. measurements. It would be conceded that E.M.F. is not a bulk property but a property depending upon the specific ion and its concentration. Any confirmatory evidence from such a source therefore is bound to be of great importance (*cf.* Part II, the system: KNO_3–$AgNO_3$–H_2O).

EXPERIMENTAL

The solutions were the same as those employed for the investigation of other physico-chemical properties already described (Parts I and III). Regarding E. M. F. measurements scrupulous care is necessary in the purification of materials for obtaining reproducible results. Pure lead electrodes did not yield consistent readings, hence amalgamated electrodes were employed. Two, or some times even three, sets of cell combination were used for the same solution in order to ensure the reproducibility and accuracy of results.

The electrode was freshly amalgamated before the commencement of each experiment. The mercury for this purpose was treated chemically, and ultimately distilled in a small pyrex distillation apparatus. The potentiometer used was a very sensitive one (supplied by W. G. Pye & Co., Cambridge) reading to 0·01 millivolt. Before and after each experiment the calibration of the potentiometer was checked against a standard Weston cell.

The following cells were investigated:—

(1)	Pb	$Pb(NO_3)_2$	KNO_3 sat.	Hg_2Cl_2 in KCl(N.)	Hg
(2)	Pb	$Pb(NO_3)_2 + KNO_3$	KNO_3 sat.	Hg_2Cl_2 in KCl(N.)	Hg
(3)	Pb	$Pb(NO_3)_2 + NH_4NO_3$	NH_4NO_3 sat.	Hg_2Cl_2 in KCl(N.)	Hg

For minimising diffusion the ends of the half cells were plugged with filter-paper wetted with solution. Three readings were taken for every solution after an interval of 15 minutes each. The significant results are tabulated in Tables I and II. For purposes of comparison the values obtained with lead nitrate alone in the absence of potassium nitrate are also recorded (Table III).

TABLE I

The system: KNO_3–$Pb(NO_3)_2$–H_2O

Room temperature : (about 20° C.)

Soln. No.	C.C.* $Pb(NO_3)_2$ added	E.M.F.	Soln. No.	*C.C. $Pb(NO_3)_2$ added	E.M.F.
	c.c.			c.c.	
1	0	0·5594	14	18	0·4446
2	2	0·4694	15	20	0·4460
3	3	0·4638	16	22	0·4430
4	4	0·4604	17	24	0·4422
5	5	0·4602	18	26	0·4414
6	6	0·4560	19	28	0·4405
7	7	0·4543	20	30	0·4395
8	8	0·4528	21	32	0·4386
9	9	0·4520	22	34	0·4376
10	10	0·4523	23	36	0·4367
11	12	0·4466	24	38	0·4357
12	14	0·4460	25	40	0·4348
13	16	0·4454			

* Refers to the number of c.c. of lead nitrate soln. (M.) added to 20 c.c. KNO_3 solution (M).

TABLE II

The system: NH_4NO_3–$Pb(NO_3)_2$–H_2O

Temperature : (about 20° C.)

(Composition of solutions same as in Table I, with NH_4NO_3 substituted for KNO_3)

Soln. No.	E.M.F.	Soln. No.	E.M.F.	Soln. No.	E.M.F.
1	0·5077	10	0·4503	18	0·4406
2	0·4663	11	0·4466	19	0·4398
3	0·4615	12	0·4454	20	0·4389
4	0·4582	13	0·4446	21	0·4379
5	0·4581	14	0·4438	22	0·4369
6	0·4540	15	0·4449	23	0·4359
7	0·4522	16	0·4423	24	0·4350
8	0·4508	17	0·4414	25	0·4341
9	0·4500				

TABLE III

The system: $Pb(NO_3)_2$-H_2O

(Composition of the solutions same as in Table I)

Soln. No.	E.M.F.	Soln. No.	E.M.F.	Soln. No.	E.M.F.
1	..	10	0·4414	18	..
2	0·4548	11	0·4405	19	..
3	..	12	..	20	0·4344
4	0·4482	13	..	21	..
5	0·4462	14	0·4375	22	..
6	0·4449	15	0·4370	23	..
7	..	16	0·4364	24	..
8	..	17	..	25	0·4321
9	0·4419				

The E.M.F. values are plotted against the corresponding concentrations of lead nitrate (Figs. 1 and 2). It may be noticed that the curve for

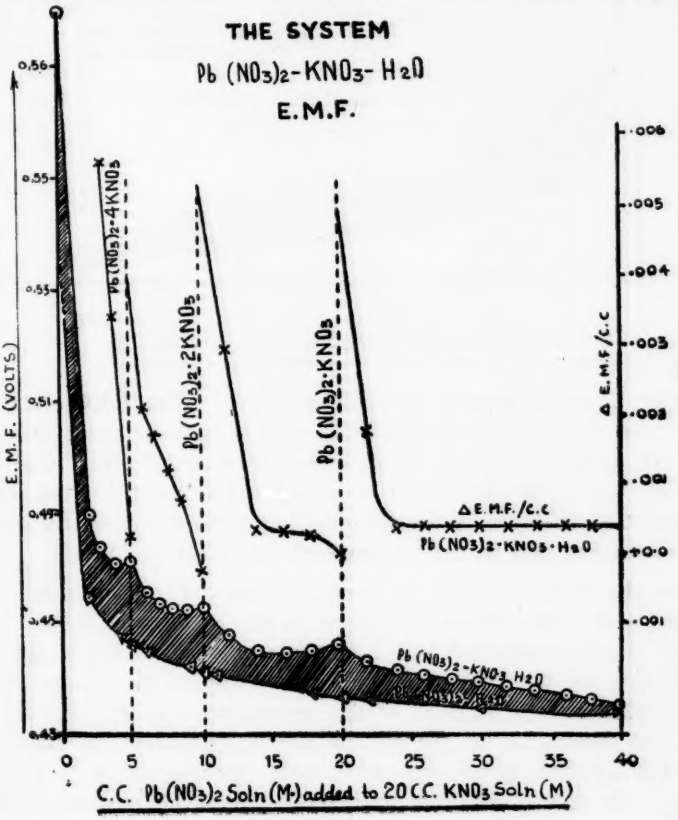

FIG. 1

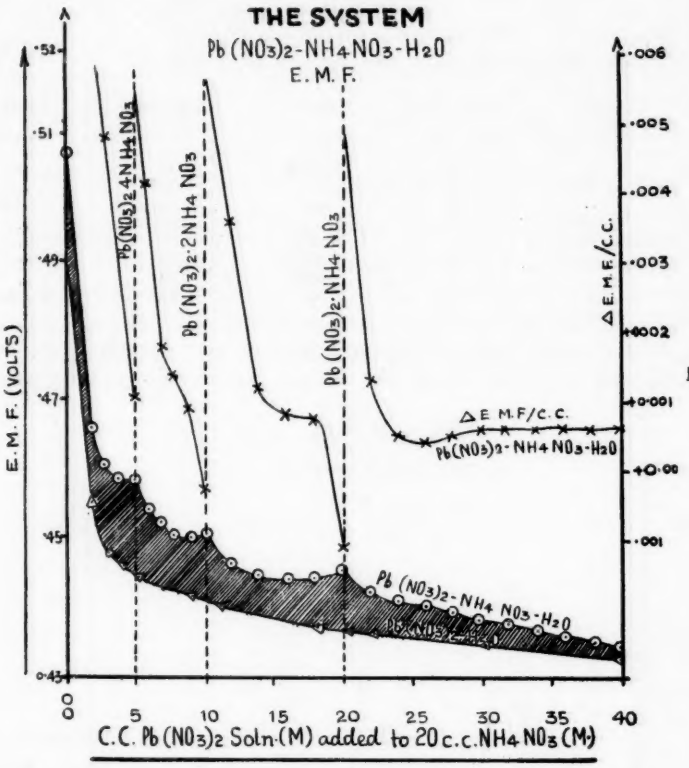

FIG. 2

lead nitrate alone is smooth without any kinks. The KNO_3–Pb $(NO_3)_2$–H_2O, as also NH_4NO_3–Pb $(NO_3)_2$–H_2O, system gives a curve with three breaks. To bring out these points more prominently the "Change of E.M.F. per c.c." (the differential variation) is also plotted, from which it will be seen that the curves at the points of inflexion become nearly asymptotic, thus indicating that we are dealing with real transition points.

From the E.M.F. curves one may visualise the changes taking place to Pb $(NO_3)_2$ or more accurately Pb ion, in the presence of KNO_3. Since the lower curve represents E.M.F. of Pb $(NO_3)_2$ alone while the upper one that of the mixture, the shaded area gives us a picture of the changes effected. Since the E.M.F. is a measure of the concentration of Pb ion, one may calculate the diminution of the Pb ion concentration on the addition of KNO_3. For example at the transition point corresponding to 20 c.c. of Pb $(NO_3)_2$, the E.M.F. changes from 0·4370 to 0·4447, which means in

the presence of KNO_3 the effective concentration of $Pb(NO_3)_2$ has been lowered from 20 c.c. to about 6 c.c., which works out to 70% diminution. Similarly at 10 c.c. and 5 c.c. the reduction effected is about 75% in each case as read from the graph. We may conclude therefore that a large percentage (70–75%) of cations (*i.e.*, Pb ion) has been converted to anions in the presence of KNO_3 or NH_4NO_3.

Conclusion

E.M.F. measurements fully support the evidences from other physico-chemical measurements, indicating the formation of three compounds of $Pb(NO_3)_2$ with KNO_3, *viz.*, $4\,KNO_3.Pb(NO_3)_2$, $2\,KNO_3.Pb(NO_3)_2$, $KNO_3.Pb(NO_3)_2$ and also three analogous compounds with NH_4NO_3, *viz.*, $4\,NH_4NO_3.Pb(NO_3)_2$, $2\,NH_4NO_3.Pb(NO_3)_2$ and $NH_4NO_3.Pb(NO_3)_2$.

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FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND ALKALI NITRATES

Part V. Transport Number Measurements

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Received September 5, 1947

(Communicated by Dr. K. S. Gururaja Doss, F.A.SC.)

In the earlier parts of this series enough experimental evidence has been adduced to indicate the probable existence of three compounds in each of the systems: KNO_3–Pb $(NO_3)_2$–H_2O and NH_4NO_3–Pb $(NO_3)_2$–H_2O. The next logical step should have been to isolate these compounds, and to obtain them in a pure state. This does not seem possible since they are unstable and exist apparently only in solution, and attempts to obtain them by evaporation result in their decomposition into the constituent salts. Microscopic examination of the residue after evaporation has not yielded unequivocal results, and it is hoped to report on this in a later paper.

We are thus left with the alternative of investigation of properties while the substance is still in solution. The centre of interest is the lead ion, and a more quantitative idea of its behaviour can be obtained by studying the *transport number* of this ion. In this paper we record the results obtained for the lead ion in the Pb $(NO_3)_2$ solution under different conditions, that is when the salt is present singly and in presence of alkali nitrates. For purposes of comparison we record similar results obtained for Ag ion in the system: KNO_3–$AgNO_3$–H_2O.

K. George Falk[1] determined the transport number of lead ion in a solution of Pb $(NO_3)_2$ and obtained the value $0 \cdot 487 \pm 0 \cdot 005$ at 25° C., which did not appreciably change with concentration. The same value was also obtained by Kohlrausch,[2] calculating it from the equivalent conductances of the separate ions.

We first made a few attempts to determine the transport number of the Pb ion following Hittorf's method, employing platinum electrodes (both anode and cathode). No reproducible results were obtained. There was evolution of gas at the anode even with a current of 2 milliamperes. The middle compartment also showed variation in composition of the solution. Further there was a black deposit formed on the anode, which on examination proved to be PbO_2. This however was not unexpected, since one of

the well-known methods of estimation of Pb depends on the anodic deposition of PbO_2.

After a few further trials we designed an apparatus (Fig. 1), which was a modified form of that described in *Pract. Phys. Chemistry* by Findlay,

TRANSPORT NUMBER APPARATUS

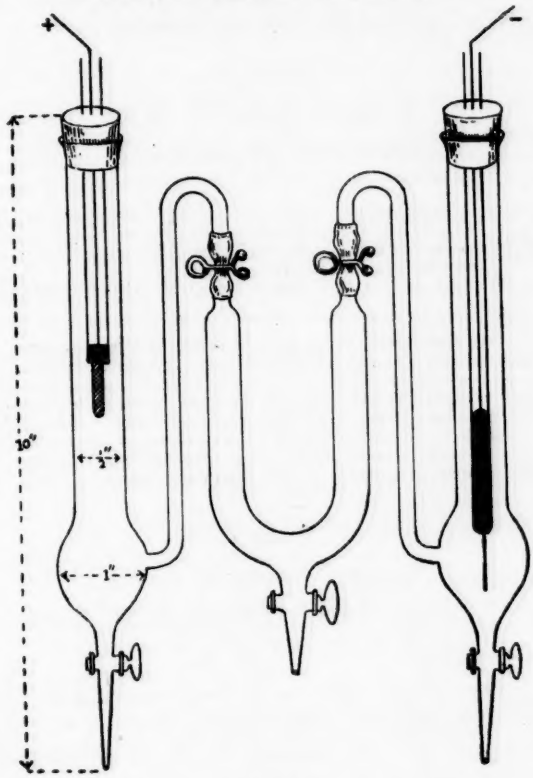

FIG. 1

the chief modification being an extension or elongation of the two side tubes, connecting the anodic and cathodic compartments to the middle U-tube. The electrodes were connected in series through a water resistance, Cu voltameter and milliammeter to the mains. The current was adjusted to 5–7 m.A. The anode was of pure lead and cathode of platinum. After passing the current for two hours, liquids were withdrawn for analysis from all the three compartments respectively. Lead was estimated as $PbCrO_4$,

as described by Falk,[1] and calculations for transport number from the anodic compartment were made by using the equation:—

$$\text{Transport number} = \frac{\text{Original concn.} + \text{Pb dissolved} - \text{Final concn.}}{\text{Pb equivalent of total current}}$$

Results obtained with the four systems: (1) KNO_3–Pb $(NO_3)_2$–H_2O, (2) NH_4NO_3–Pb $(NO_3)_2$–H_2O, (3) $NaNO_3$–Pb $(NO_3)_2$–H_2O, and (4) KNO_3–$AgNO_3$–H_2O, are given in the following tables.

TABLE I

Transport Number of Pb ion

The system: $Pb(NO_3)_2$–H_2O

Soln. No.	Concentration	Expt. No.	Wt. of Soln. (anode)	Wt. of $Pb(NO_3)_2$ after electrolysis	Wt. of H_2O (calc.)	Wt. of $Pb(NO_3)_2$ before electrolysis	Total current equivalent to		Wt. of $Pb(NO_3)_2$ migrated	Transport Number	Mean
							Cu	$Pb(NO_3)_2$			
I	(M/5) ..	(1)	29·8930	1·9208	27·9722	1·8735	0·0173	0·09014	0·04284	0·4752	0·4759
		(2)	28·4212	1·8335	26·5877	1·7877	0·0168	0·08753	0·04170	0·4764	
II	(M/10) ..	(1)	28·4940	0·9583	27·4457	0·9190	0·0144	0·07503	0·03573	0·4762	0·4777
		(2)	28·6800	0·9718	27·7082	0·9292	0·0157	0·08180	0·03920	0·4792	
III	(M/20) ..	(1)	28·0618	0·4898	27·5720	0·4612	0·0106	0·05523	0·02663	0·4814	0·4816
		(2)	27·8234	0·4949	27·3285	0·4584	0·0135	0·07034	0·03384	0·4819	

TABLE II

Transport Number of Pb ion

The system: $Pb(NO_3)_2$–KNO_3–H_2O

Soln. No.	Concentration	Expt. No.	Wt. of soln. (anode)	Wt. of $Pb(NO_3)_2$ after electrolysis	Wt. of H_2O (calc.)	Wt. of $Pb(NO_3)_2$ before electrolysis	Total current equivalent to		Wt. of $Pb(NO_3)_2$ (migrated)	Transport Number	Mean
							Cu	$Pb(NO_3)_2$			
I	M/5KNO_3 +M/5 $Pb(NO_3)_2$ Mol. Ratio (1:1)	(1)	31·6784	2·0302	29·6482	1·9730	0·0156	0·08128	0·02408	0·2962	0·2941
		(2)	29·4100	1·8930	27·5170	1·8318	0·0166	0·08649	0·02529	0·2920	
II	M/5 KNO_3 +M/10 $Pb(NO_3)_2$ Mol. Ratio (2:1)	(1)	29·4936	1·0016	28·4920	0·9406	0·0144	0·07503	0·01403	0·1870	0·1904
		(2)	28·9262	0·9952	27·9310	0·9222	0·0174	0·09066	0·01766	0·1938	
III	M/5 KNO_3 +M/20 $Pb(NO_3)_2$ Mol. Ratio (4:1)	(1)	27·5486	0·5195	27·0291	0·4500	0·0154	0·08008	0·01058	0·1320	0·1340
		(2)	28·9191	0·5445	28·3746	0·4725	0·0160	0·08336	0·01136	0·1360	

TABLE III

Transport Number of Pb ion

The system: NH_4NO_3–$Pb(NO_3)_2$–H_2O

Soln. No.	Concentration	Expt. No.	Wt. of soln. (anode)	Wt. of $Pb(NO_3)_2$ after electrolysis	Wt. of H_2O (calc.)	Wt. of $Pb(NO_3)_2$ before electrolysis	Total current equivalent to		Wt. of $Pb(NO_3)_2$ migrated	Transport Number	Mean
							Cu	$Pb(NO_3)_2$			
I	M/5 NH_4NO_3 + M/5 $Pb(NO_3)_2$ Ratio (1:1)	(1)	30·3960	1·9675	28·4285	1·9050	0·0174	0·09066	0·02816	0·3106	0·3081
		(2)	28·9060	1·8764	27·0296	1·8120	0·0178	0·09275	0·02834	0·3055	
II	M/5 NH_4NO_3 + M/10 $Pb(NO_3)_2$ Ratio (2:1)	(1)	28·3044	0·9894	27·3150	0·9112	0·0188	0·09795	0·01975	0·2016	0·2044
		(2)	29·4730	1·0242	28·4488	0·9490	0·0182	0·09483	0·01963	0·2071	
III	M/5 NH_4NO_3 + M/20 $Pb(NO_3)_2$ Ratio (4:1)	(1)	28·6852	0·5396	28·1456	0·4670	0·0165	0·08597	0·01337	0·1555	0·1509
		(2)	27·9772	0·5376	27·4396	0·4553	0·0185	0·09639	0·01409	0·1463	

TABLE IV

Transport Number of Pb ion

The system: $NaNO_3$–$Pb(NO_3)_2$–H_2O

Soln. No.	Concentration	Expt. No.	Wt. of soln. (anode)	Wt. of $Pb(NO_3)_2$ after electrolysis	Wt. of H_2O	Wt. of $Pb(NO_3)_2$ before electrolysis	Total current equivalent to		Wt. of $Pb(NO_3)_2$ migrated	Transport Number	Mean
							Cu	$Pb(NO_3)_2$			
I	M/5 $NaNO_3$ + M/5 $Pb(NO_3)_2$ Ratio (1:1)	(1)	29·5738	1·9090	27·6648	1·8550	0·0186	0·09692	0·04292	0·4430	0·4452
		(2)	30·4630	1·9620	28·5010	1·9120	0·0174	0·09056	0·04066	0·4473	
II	M/5 $NaNO_3$ + M/10 $Pb(NO_3)_2$ Ratio (2:1)	(1)	28·8030	0·9755	27·8275	0·9212	0·0176	0·09170	0·03750	0·4078	0·4093
		(2)	29·5126	1·0012	28·5114	0·9444	0·0185	0·09639	0·03959	0·4108	
III	M/5 $NaNO_3$ + M/20 $Pb(NO_3)_2$ Ratio (4:1)	(1)	28·7480	0·5185	28·2295	0·4677	0·0162	0·08441	0·03361	0·3945	0·3920
		(2)	29·1504	0·52715	28·6233	0·4743	0·0166	0·08650	0·03370	0·3895	

TABLE V

Transport number of Pb ion under different conditions

The system : $Pb(NO_3)_2$–H_2O		Molecular Ratio of Alkali nitrate to lead nitrate	The system : KNO_3–$Pb(NO_3)_2$–H_2O		The system : NH_4NO_3–$Pb(NO_3)_2$–H_2O		The system : $NaNO_3$–$Pb(NO_3)_2$–H_2O	
Concn.	Transport No.		Transport No. (mean)	% change	Transport No. (mean)	% change	Transport No. (mean)	% change
M/5	0·4759	(1:1)	0·22942	38·18%	0·3081	35·3%	0·4452	6·4%
M/10	0·4777	(2:1)	0·1901	60·2%	0·2044	57·2%	0·4093	14·32%
M/20	0·4816	(4:1)	0·1340	72·2%	0·1509	68·7%	0·3920	18·6%

TABLE VI

Transport Number of Ag ion

The system: $AgNO_3$–H_2O

Concentration of $AgNO_3$ Solution: (M/10)

Expt. No.	Wt. of soln.	Wt. of $AgNO_3$ after electrolysis	Wt. of H_2O (calc.)	Wt. of $AgNO_3$ before electrolysis	Total current equivalent to		Wt. of $AgNO_3$ (migrated)	Transport Nhmber	Mean
					Cu	$AgNO_3$			
I	27·7697	0·5164	27·2533	0·4690	0·017	0·09086	0·04346	0·4783	0·4796
II	26·4076	0·4909	25·9167	0·4460	0·016	0·08657	0·04167	0·4813	

TABLE VII

Transport Number of Ag ion in presence of KNO_3

The system: KNO_3–$AgNO_3$–H_2O

Soln. No.	Concentration	Expt. No.	Wt. of soln.	Wt. of $AgNO_3$ after electrolysis	Wt. of H_2O	Wt. of $AgNO_3$ before electrolysis	Total current equivalent to		Wt. of $AgNO_3$ migrated	Transport Number	Mean
							Cu	$AgNO_3$			
I	M/10 KNO_3+ M/10 $AgNO_3$ Ratio (1:1)	(1)	27·5813	0·5453	27·0360	0·4610	0·0218	0·1165	0·03225	0·2767	0·2766
		(2)	27·9566	0·5555	27·4011	0·4673	0·0228	0·1219	0·03370	0·2765	
II	M/5 KNO_3+ M/10 $AgNO_3$ Ratio (2:1)	(1)	27·8588	0·5070	27·3518	0·4652	0·0106	0·0566	0·01486	0·2623	0·2631
		(2)	25·5600	0·5224	25·0376	0·4257	0·0246	0·1315	0·03470	0·2638	
III	M/2·5 KNO_3+ M/10 $AgNO_3$ Ratio (4:1)	(1)	29·3244	0·5572	28·7672	0·4875	0·0174	0·0930	0·02330	0·2505	0·2502
		(2)	28·1986	0·5707	27·6279	0·4102	0·0256	0·1368	0·03420	0·2500	

TABLE VIII

The percentage change calculated for Ag ion in presence of potassium nitrate at different concentrations is given below, the value for Ag ion in absence of KNO_3 being taken as: 0·4796 (Table VI).

Soln. No.	Concentration	Transport Number	Percentage
I	M/10 KNO_3+M/10 $AgNO_3$ Ratio (1:1)	0·2766	42·33%
II	M/5 KNO_3+M/10 $AgNO_3$ Ratio (2:1)	0·2631	45·14%
III	M/2·5 KNO_3+M/10 $AgNO_3$ Ratio (4:1)	0·2502	47·83%

Table I gives the results for $Pb(NO_3)_2$ alone at three concentrations (M/5, M/10 and M/20) while Table II gives the results for the same concentrations of $Pb(NO_3)_2$ but in the presence of KNO_3, the concentrations being such that the stoichiometric ratios 1 : 1, 1 : 2 and 1 : 4 are maintained. Tables III and IV are repetitions of Table II, with the substitution of NH_4NO_3 and $NaNO_3$ respectively in place of KNO_3. Table V gives the summarised results, and percentage (%) change noted under different conditions. Tables VI, VII and VIII, list the results obtained for the transport number of Ag-ion in $AgNO_3$ solution under similar conditions.

DISCUSSION

The summarised results in Table V are worthy of close study. The figures obtained for KNO_3 and NH_4NO_3 are of the same order of magnitude, the maximum change with an excess of alkali being about 70%. $NaNO_3$, on the other hand, shows a maximum change of only 18%. This latter may be interpreted to mean some tendency for the formation of complex ions as originally pointed out by Lewis,[3] on the basis of E.M.F. measurements. But definite complexes obeying stoichiometric laws do not seem to exist in this system.

The larger variations of the transport number of the Pb-ion in the presence of KNO_3 or NH_4NO_3 can be explained only on the assumption of formation of definite complexes, and we may obtain a clearer idea of these by comparing the figures for the KNO_3–$AgNO_3$–H_2O system, where one complex may be presumed to exist when the ratio of concentrations is 1 : 1 (Tables VI, VII and VIII).

Ratio of Concn. KNO_3 : $AgNO_3$ or : $Pb(NO_3)_2$	Change of transport number of cation	
	$AgNO_3$	$Pb(NO_3)_2$
1 : 1	42·33 %	38·12 %
2 : 1	45·14 %	60·20 %
4 : 1	47·83 %	72·20 %

When the molecular ratio of the two salts is 1 : 1 the figures representing the change of transport number are of same order of magnitude. Any further increase in the concentration of KNO_3 does not seem to affect the transport number of Ag ion very much, signifying that there is no further complex formation. The percentage changes in the case of Pb ion are of a totally different order of magnitude, which are quite in keeping with the evidences already available for the formation of three complexes.

The very large changes in the values of transport number of Pb-ion may also be compared to the percentage (%) diminution of Pb ion concentration observed in the E.M.F. experiments (*vide* Part IV of the series). The effective concentration of $Pb(NO_3)_2$ was found to be diminished by about 70–75% in presence of KNO_3, which meant that this much amount of cation had been converted to anions.

Conclusion

The results obtained with the experiments on transport number indicate:

(1) significant variations in the value for Pb ion in presence of KNO_3 or NH_4NO_3;

(2) three different orders of magnitude in the values corresponding to the three different complexes assumed to exist in solution; while

(3) the value for Ag ion in presence of KNO_3 shows a very sharp change for a ratio of molecular concentrations 1 : 1, but no significant change for any further increase in the concentration of alkali nitrate, signifying that we are here dealing with only one complex compound, and

(4) sodium nitrate affects the transport number of Pb ion to some extent showing a slight tendency for the formation of complexes, but no stoichiometric relations have been observed.

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OPTICALLY POSITIVE CORDIERITE FROM THE KHONDALITES OF PACHIPENTA, VIZAGAPATAM DISTRICT

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The occurrence of cordierite in the khondalites of Vizagapatam District was reported by Walker (1900), and Middlemiss (1904). Walker and Collins (1907) recognized four types of cordierites in the area but they did not give any analysis of the mineral or its detailed optical characters. Chacko (1916) described an optically positive cordierite from Travancore and gave analysis of selected grains of the mineral. He quotes in the paper G. De P. Cotter's note which refers to a solitary case of an optically positive cordierite from the khondalites of the Vizagapatam District. M. S. Krishnan (1924) described an optically positive cordierite collected by Prof. T. N. Muthuswami from Madura District. L. A. N. Iyer (1929) also recorded the occurrence of an optically positive cordierite from the para-gneisses of Coimbatore. A few foreign occurrences of optically positive cordierite have been reported by Rutherford (1933 and 1936) from Canada, Conant (1935) from New Hampshire, U.S.A., and Folinsbee from Great Slave Lake area (1941). Only some of the authors, however, give analysis for the mineral.

During the course of the systematic studies on the Eastern Ghat ranges undertaken by the Geology Department of the Andhra University, a beautiful blue mineral occurring as lenses, pockets and streaks at the foot of the hill Δ 1379 in Pachipenta Zamindari (between Lat. 18° 26′ and 18° 32′ and Long. 83° 3′ and 83° 10′) was collected by one of us (G. G. K. S.) from the khondalites and this paper records the results of a chemical and optical examination of the mineral. The rock in which the mineral occurs is fresh and compact and consists of folia of quartz, felspar, and cordierite, alternating with those of garnet, and sillimanite. The formations here have a W.N.W. strike and a S.S.W. dip. the amount of dip being about 30°–35°. The cordierite has a rich blue colour in transmitted light. Its hardness is 7·5 and Sp. Gr. 2·71. It is colourless in thin sections; however in slightly thicker sections, it has a delicate blue colour and it is pleochroic from pale blue to deep blue. The birefringence is very weak and the mineral polarises in first order greys. The optic axial angle ' 2V ' as measured by Fedorov's

Stage is 74° and unlike the normal cordierite, it is optically positive. It may here be recorded that '2V' for the optically positive cordierite from Madura ranges from 81°–85°, for the cordierite from Travancore it is about 90°, and for the cordierite from Great Slave Lake, about 85°. The micro-sections reveal the presence of pleochroic haloes around zircon nuclei. The pleochroic haloes are most brilliant for a certain vibration direction of the mineral and disappear completely on the section being rotated through 90°. Sometimes the cordierite shows polysynthetic twinning resembling that of plagioclase felspar, but distinguished from the latter by the fact that the twin planes intersect each other at small angles. The cordierite occasionally shows regularly arranged inclusions, sillimanite being one of these.

The chemical analyses and molecular proportions of this optically positive cordierite with the available analyses of cordierites from other localities, are given in Table I.

TABLE I

	A		B		C		D		D	
Locality	Pachipenta		Madura		Travancore		Standard		Grate Slave Lake	
Constituents	Wt. %	Mol. Prop.	Wt. %	Mol. Prop.	Wt. %	Mol. Prop.	Wt. %	Mol. Prop.	Wt. %	Mol. Prop.
SiO_2 ..	48·33	805	48·37	806	49·74	829	49·40	823	48·19	802
Al_2O_3 ..	32·31	317	29·22	286	35·21	345	33·60	329	33·45	328
Fe_2O_3 ..	2·22	14	2·20	14	5·65	36	..	..	0·55	3
FeO ..	3·74	52	7·07	99	3·00	42	5·30	74	8·40	117
MgO ..	10·66	267	9·54	239	4·30	108	10·20	255	7·95	197
MnO ..	..	..	0·42	6	..	..	..	..	0·18	3
CaO ..	0·84	15	1·92	34	1·05	20	..	..	0·17	3
Na_2O ..	..	..	..	..	..	..	..	..	0·22	3
K_2O ..	..	..	..	..	..	..	..	..	0·02	0
Li_2O ..	..	..	..	..	..	..	..	..	Trace	0
TiO_2 ..	..	..	..	..	..	..	..	..	0·01	0
H_2O- ..	1·44	80	1·84	102	1·74	97	1·50	83	0·01	0
H_2O+									0·67	37
Total ..	99·54		100·58		100·69		100·00		99·82	
Mol. Ratio Mg/Fe	5·1		2·4		2·6		3·4		1·6	
2V ..	74°		81°–84°		90°		70°–25′		83°	
Optical sign ..	Positive		Positive		Positive		Negative		Positive	
Sp. Gr. ..	2·74		2·598		3·0–2·6		2·6–2·66		2·631	

A : Cordierite from Pachipenta, Analyst : G. G. K. Sastri.
B : Cordierite from Madura Dist. Analyst : M. S. Krishnan (*Mineral Mag.*, 1924, p. 249).
C : Cordierite from Travancore, Analyst : Chacko (*Geol. Mag., London*, 1916, pp. 462–64).
D : Cordierite from Dana's *Text-Book of Mineralogy*.
E : Cordierite from Great Slave Lake, Analyst : Folinsbee (*Am. Min.*, 1941, **26**, p. 487).

The molecular proportions of the cordierite from the Pachipenta area are as follows:

Constituents	Mol. Prop.		
SiO_2	805	805	SiO_2
Al_2O_3	317	331	$(Al, Fe)_2O_3$
Fe_2O_3	14		
FeO	52	319	(Mg,Fe)O
MgO	267		
CaO	15	50	CaO
H_2O	80	80	H_2O

The molecular formula of the mineral is 15 CaO 319 (Mg, Fe) O 331 Al, Fe)$_2O_3$ 805 SiO_2 80 H_2O.

When the formula is simplified it comes to 4 (Mg, Fe) O 4 (Al, Fe)$_2$ O_3 10 SiO_2 H_2O, and this corresponds closely to that of the cordierite as given by Dana (1922). It will be seen from analyses (A) that some Fe_2O_3 is isomorphous with Al_2O_3. A very slight excess of Al_2O_3 and SiO_2 can also be noted. This is apparently due to the presence of small amounts of sillimanite in the mineral as inclusions.

The molecular formula of the cordierite from Madura as calculated by Mahadevan (1927) from Krishnan's analysis is 32 SiO_2 12 Al_2O_3 15 (Fe, Mg) O 4 H_2O.

Discussion

The relationship between chemical composition and optical properties is still one of the unsolved problems of mineralogy. To account for the anomalous optical sign of the mineral from Madura, Krishnan (1924, p. 250) remarks " what seems to be highly probable is that the isomorphous replacement of MgO by FeO may produce a change in the value of the optical axial angle imparting the positive optical character to the cordierite ". He refers in this connection to the parallel cases of enstatite-hypersthene and forsterite-fayalite series where the ratio of MgO to FeO determines the sign and value of the optic axial angle. The cordierite from Madura (B) contains MgO 9·54% (Mol. Prop. 239) and FeO 7·07% (Mol. Prop. 99) and the cordierite from Travancore (C) MgO 4·30% (Mol. Prop. 108) and FeO 3·0% (Mol. Prop. 42). The Mol-ratio of MgO to FeO in these is 2·4 and 2·6 respectively. The cordierite from Pachipenta shows MgO 10·66% and FeO 3·74% that is the Mol-ratio of MgO to FeO is 5·1. It is thus seen that the reason given as probable by Krishnan does not really find support from the analysis of the cordierite from Pachipenta where FeO is as low as 3·74% and MgO is 10·66% and the Mol-ratio of MgO to FeO is as high as 5·1

in contrast to the corresponding Mol-ratios of 2·4 and 2·6 for the cordierites from Madura and Travancore. The Mol-ratio of MgO to FeO for normal corderite according to Dana is about 3·4. It might be stated here that the cordierite used in this study from Pachipenta was from a lenticular mass about 2″ × 3″ and the positive character of this cordierite was consistent for all the sections made from it and the chemical analysis of the mineral was carried out from the same specimen.

Reference to the analogy of the enstatite-hypersthene and forsterite-fayalite series is applicable only in so far as there is a change in optical sign and optical axial angle with the change in the ratio of MgO to FeO. In those cases the minerals free from FeO give an optically positive sign and with increase of FeO the optical axial angle changes and the sign becomes negative, *i.e.*, precisely the reverse of the case of cordierite from Madura and Travancore where the negative sign is changed to positive with the greater proportion of FeO. In the case of cordierite from Pachipenta however the parallel of enstatite-hypersthene, forsterite-fayalite series seems to apply satisfactorily. As the available data are too few, all that we can say is that the change in optical sign of the mineral does not appear to be due to the Fe/Mg ratio. Winchell (1937) too records the unsuccessful attempts to obtain a reasonable correlation of composition based on FeO and MgO ratios and optical properties in cordierites from published data. He refers to the work of Shibata and finds that the correlation between chemical composition and optical properties does not show close correspondence whereas there is a closer relationship between Sp. Gr. and optical properties in cordierites, though this correspondence is by no means universal. Folinsbee (1941) in an interesting paper describes an optically positive cordierite from north of the Great Slave Lake, in a rock associated with an injection and assimilation gneiss consisting of cordierite, garnet, sillimanite, spinel, graphite, biotite, orthoclase, microcline, oligoclase felspar, quartz and tourmaline. In analogy with the known variations in the structure of beryls in relation to their alkali contents, Folinsbee suggests that the alkalies have a pronounced effect on the structure and optical properties of cordierites. From the data available for Indian cordierites it is not possible to say how far this explains the anomalous character of cordierite as no alkalies have been reported from any of these.

Summary and Conclusion

An optically positive cordierite from the khondalites in Pachipenta of Vizagapatam District was chemically analysed and its optical properties determined. It has a hardness of 7·5 and Sp. Gr. 2·71 and its 2V as

determined by Fedorov's Stage is 74°. In contrast to the negative optical sign of a normal cordierite, this cordierite gives a positive optical sign. The tentative suggestion put forward by Krishnan and others that the optically positive character of cordierites is probably due to the ratio of MgO to FeO does not find support from the present studies. As shown by Winchell it appears that there is no close correspondence between chemical composition and optical characters in cordierites. The possibilities of traces of alkalies contributing to the change in optical sign, as suggested by Folinsbee, is worth consideration but must await the availability of analyses giving these constituents.

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INTERACTION OF CARBON MONOXIDE AND HYDROGEN UNDER SILENT DISCHARGE: PRODUCTION OF FORMALDEHYDE

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Thermochemical interaction of carbon monoxide and hydrogen investigated by numerous workers has led to products of some technical importance, *viz.*, a number of saturated and unsaturated hydrocarbons,[1] methyl alcohol,[2] etc. It has been found that the above mixture when subjected to an electric discharge shows a pronounced tendency towards condensation. Thenard and Brodie[3] obtained chiefly methane and some complex oily products. The detection of formaldehyde amongst the above reaction products is due to Losanitsch and Jovitschitsch,[4] and especially Lob[5] and Koenig and Weinig.[6] No quantitative information is available in the literature for the occurrence of the above reaction. Most workers formulated the formation of various complex products from formaldehyde produced as a product of primary reaction. It appeared, therefore, that if the primary products were removed from the sphere of reaction to prevent secondary changes and polymerisations, it might be possible to utilise this process for the preparation of formaldehyde. This has now been achieved by circulating the gases through the reaction vessel and scrubbing off the soluble products.

Apparatus

The apparatus used in the preliminary stages of this work[7] consisted of a system of two to six ozonisers connected in parallel and fed by a mixture of carbon monoxide and hydrogen kept in circulation by a 'Cenco' hyvac pump. The effluent gases from the ozonisers were returned to the gas reservoir after washing them off the soluble products. The experiments were conducted at constant volume and as the gas mixture suffered condensation during the progress of the reaction, a considerable fall in the pressure resulted. This fall has been found to reduce appreciably the rate of the reaction. Only detectable quantities of formaldehyde resulted. No

improvement in yield could be brought about by the application of catalysts or by altering the rate of circulation. The apparatus was therefore modified to work at constant pressure.[8]

The circuit and the arrangement adopted finally are shown in Fig. 1. It consisted chiefly of a reservoir system and an arrangement for the circulation of the gas mixture. The former served for storing the gases and also

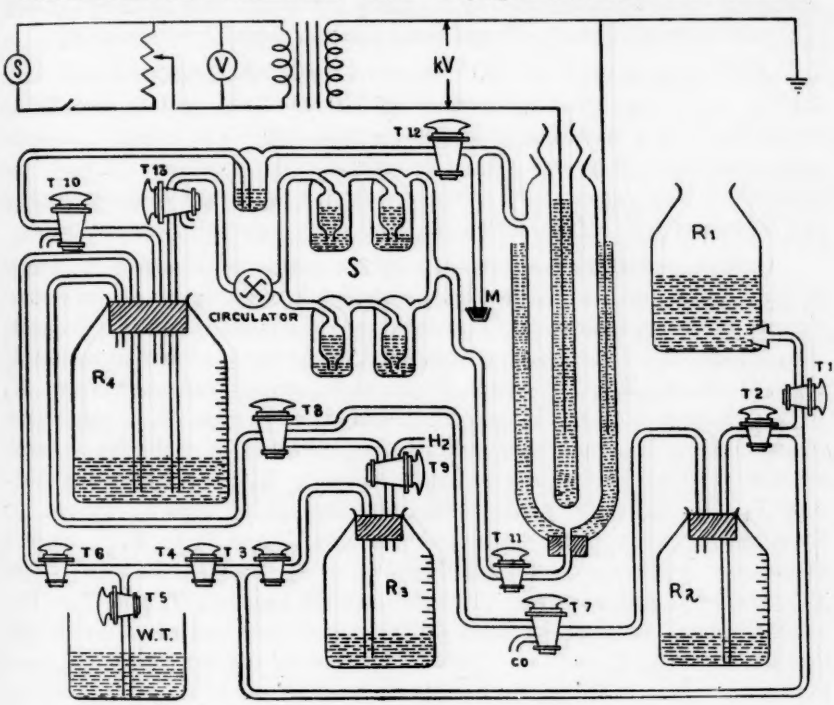

FIG. 1

for preparing a mixture of the two in the desired proportion and consisted of four reservoirs R_1, R_2, R_3 and R_4 and a water trough W. T. connected with one another by means of glass-stoppers. R_1 was placed on a higher level than the other reservoirs; as a result water flowed from it to any other part of the reservoir system. R_2 and R_3, each graduated and of 13 litres capacity and R_4 also graduated and of 2·6 litres capacity served for storing carbon monoxide, hydrogen and the gas mixture respectively. By admitting water from R_1, gas from any of the reservoirs R_2, R_3 or R_4 could be displaced.

The circulation system was a closed one in which the gas mixture was kept in constant circulation at a uniform rate at atmospheric pressure. It included the mixture reservoir R_4, a Siemens' glass ozoniser, a mercury manometer M, a system of water wash traps (S) and a circulator, connected serially. A 'Cenco' hyvac pump with its suction end connected to the water traps and the exhaust end to the reservoir served to circulate the gases. It could also be used for evacuating parts of the circulatory system. By changing the potential applied to the pump, its speed could be altered at will. The rate of circulation at different potentials was determined separately.

Alternating current of 500 cycles frequency obtained by means of a 2 kVA motor alternator set worked off 220 volt D.C. mains, was fed to the primary of a transformer of step-up ratio 150. The primary potential was regulated by means of a variable resistance in its primary. One of the secondaries was earthed; the other was dipped in the salt solution forming the inner electrode of the ozoniser. The other electrode was earthed.

Carbon monoxide was prepared by the action of hot conc. sulphuric acid on oxalic acid and purified by repeatedly passing through a strong solution of potassium hydroxide. R_2 which had been filled with water from R_1 through the taps T_1 and T_2 was connected to the stock of carbon monoxide through the tap T_7. The water displaced by carbon monoxide from R_2 passed through the taps T_4 and T_5 to the water trough W.T. Hydrogen obtained from a commercial cylinder was purified by bubbling through alkaline pyrogallol solution and was admitted to R_3 by operating the stopcock T_9. R_4 was initially filled with water through the taps T_1, T_4 and T_6. By admitting water from R_1 through the taps T_1 and T_2 to R_2, a desired quantity of carbon monoxide was displaced to R_4, through the taps T_7 and T_8. Similarly, hydrogen was displaced through the taps T_8 and T_9. The water displaced from R_4 in filling up these gases was carried to the trough through the taps T_6 and T_5. Thus a mixture of carbon monoxide and hydrogen in the desired proportion could be obtained in R_4. The tap T_{10} was closed and the ozoniser and the scrubbers were evacuated with the help of the circulator through the three-way tap T_{13}. An experiment was commenced only after the entire assembly was tested for vacuum; and after rinsing it repeatedly with the reaction mixture. R_4 was then included in the circuit by opening the taps T_{10} and T_{13}. With the gases circulated and exposed to the discharge in the ozoniser excited at the desired potential, R_4 was connected to the water trough W.T., through the taps T_6 and T_5. This served to maintain a constant pressure regime in the part of the system subjected to the circulation of the reaction mixture. Volume changes were noted by observing the level of water inside the reservoir from time to time.

At the end of an experiment, the water from the traps was collected, measured and estimated for formaldehyde, by Romijn's potassium cyanide method.[9] The results of a typical analysis are as follows (*vide* Table I, Expt. No. 3). 100 c.c. of the solution was mixed with 20 c.c. of say N/20 KCN. This was then added to 25 c.c. of N/20 $AgNO_3$, acidulated with HNO_3. The excess of this last was titrated against N/20 NH_4CNS. The required volume was 19·5 c.c.

By a previous titration, it was found that a mixture of 25 c.c. of $AgNO_3$ and 20 c.c. of KCN required 2·4 c.c. of NH_4CNS. The 100 c.c. of formaldehyde solution was therefore equal to (19·5–2·4) 17·1 c.c. of NH_4CNS. Formaldehyde present is, therefore, 0·046 gm.

Results and Discussion

Influence of Composition of the Gas Mixture.—Pure carbon monoxide also suffered condensation under silent electric discharge.[10] It appeared, therefore, that if the gas mixture contained a greater proportion of hydrogen, it might favour the reaction of carbon monoxide and hydrogen.

At a constant rate of circulation of 8 litres of reaction mixture per minute, with an applied potential of 9·6 kV and 500 cycles, experiments were conducted with gas mixtures in the ratio of 1 : 0·5 to 1 : 3 of carbon monoxide and hydrogen respectively. All the experiments were conducted for a period of six hours exposure to discharge. The results are shown in Table I and (in part with reference to the net amount of formaldehyde

Table I. *Influence of the Composition of the Gas Mixture*

Expt. No.	Ratio $CO:H_2$ (% of CO in the mixture)	Volume in c.c. of gases circulated (wt. in gm.)	Volume reduction in c.c.	Yield of formaldehyde		
				c.c. of NH_4CNS N/20	in gm.	Percentage
1	2	3	4	5	6	7
1	1 : 0·5 (66)	2800 (2·238)	780	22·0	0·033	1·51
2	1 : 0·9 (52·5)	3140 (2·035)	785	31·0	0·046	2·23
3	1 : 1 (50)	2730 (1·711)	670	30·5	0·046	2·7
4	1 : 1·5 (40)	3100 (1·574)	575	24·7	0·037	2·4
5	1 : 2 (33)	2860 (1·261)	660	23·9	0·036	2·84
6	1 : 3 (25)	2900 (1·024)	785	21·1	0·032	3·1

formation and that expressed as a percentage of the mass of the original mixture) graphically in Fig. 2.

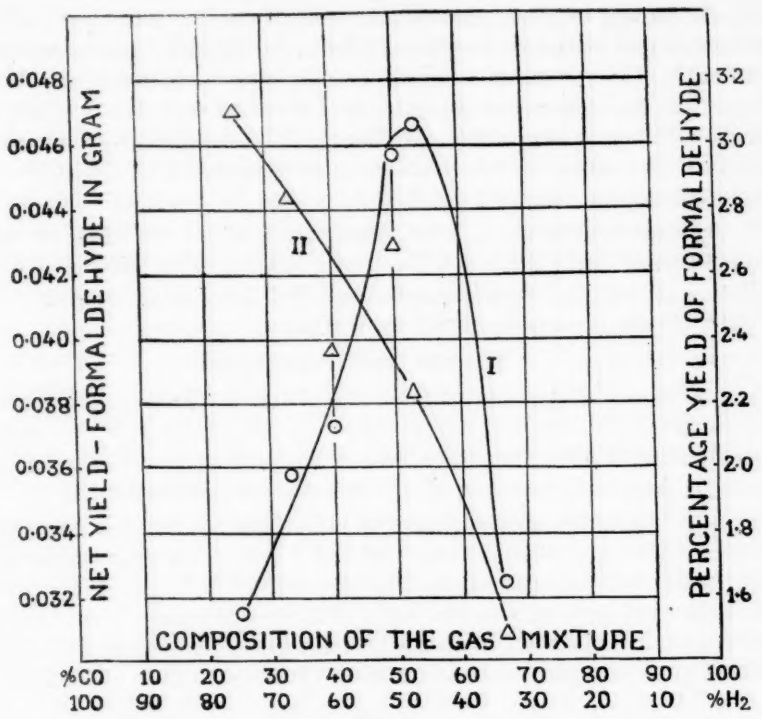

FIG. 2

The absolute yield, *viz.*, 0·046 gm. obtained was highest with an approximately equimolecular mixture of the constituent gases (Fig. 2, Curve 1). The results of experiments 4, 5 and 6 show that the yield of formaldehyde falls with an increased proportion of hydrogen in the mixture although the total reaction between the gases has been greater as shown by the reduction in gas volume (column 4). This may be attributed to an extended hydrogenation of formaldehyde—the product of primary reaction.

In contrast with the above results, the percentage yield (column 7), *i.e.*, the amount of formaldehyde expressed as percentage of the total weight of the gases circulated (column 3) shows a linear dependence with the proportion of hydrogen in the mixture (Fig. 2, Curve 2). The anomaly is only apparent, because an increased proportion of hydrogen results in a corresponding decrease in the proportion of carbon monoxide—the heavier constituent—thereby lowering the weight of the starting materials. Thus, a smaller weight of formaldehyde when represented as percentage of a relatively very much smaller weight of gas mixture appears greater. For instance,

the yields of formaldehyde in experiments 5 and 6 are 0·036 and 0·032 gm. respectively. Expressed as percentages of the initial weight of gases used, *viz.*, 1·261 and 1·029 gms. respectively, these figures appear as 2·84 and 3·1%.

At lower concentrations (column 2) of carbon monoxide, a larger proportion of it is converted into formaldehyde. This is indicated by the increased percentage yield figures. In experiments 3 to 6, where the concentration of carbon monoxide in the mixture is reduced from 50% to 25%, the percentage yield increases from 2·7 to 3·1%. The increase is, however, of little practical significance because for a comparatively small increase, a relatively large proportion of the gas mixture is lost in the form of secondary products.

The results of experiments 1 and 2, in which a larger proportion of carbon monoxide is used, in general, support the above conclusions.

It appears, from the above results, that the presence of very large excesses of one or the other of the constituents affects the yields adversely. At higher concentrations of hydrogen, secondary hydrogenation of carbon monoxide or/and formaldehyde probably takes place; with an excess of carbon monoxide, self condensation occurs lowering considerably the possibility of the reaction $CO + H_2 \rightarrow HCHO$.

Influence of the Rate of Circulation.—Behaviour of carbon monoxide-hydrogen mixtures in sealed ozonisers indicated that the rate of the reaction is maximum in the early stages of the discharge. It appeared that there was an optimum duration of exposure. As this latter could be varied by changing the rate of gas flow, an attempt was made to determine the appropriate circulation rate.

Experiments were conducted with gas mixtures in 1:1 ratio, at an applied potential of 9·6 kV and 500 cycles frequency with circulation rates of 8, 12, 14 and 24 litres per minute. The results are shown in Table II.

TABLE II. *Influence of the Rate of Circulation*

Exp. No.	Rate of circulaion litres per min.	Wash traps in series	Mercury level in the manometer in mm. (pressure in the ozoniser)	Volume of the gases c.c. (Wt. in gm.)	Reduction volume c.c.	Yield of formaldehyde	
						In gm.	Percentage
1	2	3	4	5	6	7	8
1	8	2	25 (735)	2730 (1·711)	670	0·046	2·7
2	12	2	35 (725)	2800 (1·714)	630	0·036	2·1
3	14	3	60–70 (690–700)	3000 (1·836)	775	0·041	2·2
4	24	3	160–170 (590–600)	2980 (1·822)	470	0·031	1·7

As indicated by the reduction in volume and the yield of formaldehyde in experiments 1 and 2, and 3 and 4, an increased rate of circulation, above 8 litres per minute does not favour the production of formaldehyde.

Preliminary results[8] suggested that the efficiency of the removal of formaldehyde from the gases falls off at higher rates of circulation. Experiments 3 and 4 were therefore conducted with three wash traps instead of two, used previously. The yield of formaldehyde in experiment 3 is higher than that of experiment 2, although in the former case, the rate of circulation is greater.

It will be seen (Table II, column 4) that at higher rates of circulation, the operative pressure inside the ozoniser falls progressively, owing to the increased suction. For instance, in experiment 1, it is 735 mm. whereas in experiment 4, it is about 600 mm. It is probable that this diminution in the operative pressure may be a factor contributing to lower yields at higher rates of circulation (*cf.*, Influence of Potential).

Influence of the Size of the Ozoniser.—An increased rate of circulation diminishes the duration of exposure to discharge but interferes with the absorption of formaldehyde (*vide supra*). It appeared, that at a constant rate of circulation, a variation in the length of the ozoniser would change the former without affecting the latter.

Experiments were conducted with 6″, 9″ and 12″ long ozonisers with a circulation rate of 8 litres/minute, 9·6 kV and 500 cycles frequency. The results are shown in Table III.

TABLE III. *Influence of the Size of the Ozoniser*

Expt. No.	Length of the ozoniser inches	Volume of the gases c.c. (wt. in gm.)	Reduction in volume c.c.	Yield of formaldehyde	
				in gram	Percentage
1	2	3	4	5	6
1	6	3000 (1·809)	425	0·031	1·72
2	9	3000 (1·848)	640	0·035	1·91
3	12	3000	695		

A decrease in the ozoniser length is tantamount to an increase in the rate of circulation. It is to be expected from the results of Table II that the yield of formaldehyde should fall with the length. The experimental results are in accord with this deduction. It is interesting to observe, however, that although the reduction in volume in experiment 2 is greater by

about 50% than in experiment 1, the increase in the yield of formaldehyde is only 14%. This is in agreement with the earlier conclusion (*vide* Influence of rate of circulation) that a greater duration of exposure to discharge results in the destruction of formaldehyde initially formed.

It is felt that further work is necessary to define optimum conditions with respect to the size of the ozoniser.

Influence of Excitation Potential.—According to Joshi,[11] the quantity $V-V_m$ only is significant for a discharge reaction, V and V_m being the applied and threshold potentials respectively. As a general observation, it has been known that an increase in $V-V_m$ results in an increased rate of reaction. Experiments were carried out at 6·0, 6·75, 7·5, 9·6 and 10·5 kV of 500 cycles frequency at a gas flow of 8 litres per minute. The results are shown in Table IV.

TABLE IV. *Influence of Excitation Potential*

Expt. No.	Applied potential kV	Duration of the discharge in min.	Volume of the gases c.c. (wt. in gm.)	Reduction in volume c.c.	Yield of formaldehyde	
					in gm.	Percentage
1	2	3	4	5	6	7
1	6·0	120	2800	..	..	..
2	6·75	120	2800	..	..	..
3	7·5	120	2870	210	..	..
4	9·6	360	2730 (1·711)	670	0·046	2·7
5	10·5	360	2770 (1·698)	725	0·037	2·17

It will be seen that below the threshold potential of 7·5 kV, there is no reaction. In experiments 4 and 5, the reductions in volume are 665 and 725 c.c. respectively. Thus the overall reaction velocity is greater at 10·5 kV than 9·6 kV as is to be expected. The yield of formaldehyde, on the other hand, is found to be greater by about 25% at the lower exciting potential. It is suggested, therefore, that the formaldehyde initially formed undergoes secondary changes to a greater extent at higher applied potentials.

It is probable that in experiments, where the rate of circulation is varied, a fall in the operative gas pressure (*vide supra*, Table II, column 4) resulted in a lowering of the V_m and consequently in an increase of $V-V_m$. This would have an unfavourable effect on the yield of formaldehyde and may, in fact, be a factor contributing to the observed decrease at higher rates of circulation.

The authors welcome this opportunity of expressing their sincere and grateful thanks to Professor S. S. Joshi, D.Sc. (London), F.A.Sc., F.R.I.C., Head of Chemistry Department, for suggesting the problem, instructive advice and kind encouragement during this work; and to Lala Gurucharan Lal of Messrs. Bhadani Bros., Ltd., Calcutta, for a research grant which defrayed part of the expenditure in this work.

Summary

Production of formaldehyde by the interaction of carbon monoxide and hydrogen under silent discharge at 500 cycles frequency has been investigated with respect to (1) the gas composition, (2) the rate of circulation, (3) the ozoniser size and (4) the excitation potential. The gas mixture was circulated through the reaction vessel at atmospheric pressure and formaldehyde was removed from the effluent gases by scrubbing through water wash traps. The optimum values for formaldehyde formation in respect of factors 1 to 4 have been determined. An increase above this value of 2 decreases the yield due to (in part) incomplete absorption of the product. A larger ozoniser size increases the net yield but entails a waste of the reacting mixture. Increase of the excitation potential increases the velocity of the change but reduces the yield due to secondary changes in the formaldehyde produced. Equimolecular mixtures of the reacting gases with optimum values under 2, 3 and 4 correspond to 0·046 gm., *i.e.*, 16 gm. per KW-hour.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XII. Constitution and Synthesis of Pedicin and Its Allies

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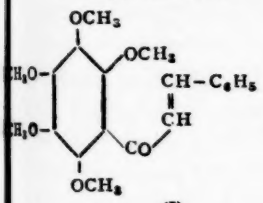
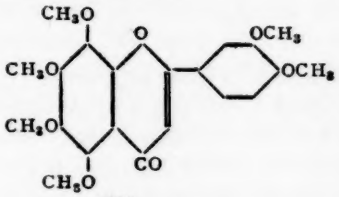
PEDICELLIN[1] (I) is an important member of the chalkone group having a fully oxidised and methylated benzene ring and in this respect it is analogous to nobiletin (flavone, II) and calycopterin (flavonol, III). In connection with our study of the toxic properties of chalkones towards fish,[2] we had occasion to prepare it from the leaves of *Didymocarpus pedicellata*. In the course of his careful work Siddiqui[1] obtained from this source besides pedicellin the related compounds pedicin, isopedicin and pedicinin. Using a modification of the extraction procedure we have now been able to isolate some quantity of methyl pedicinin also and this is of significance as it indicates a stage in the formation of pedicinin.



(I)



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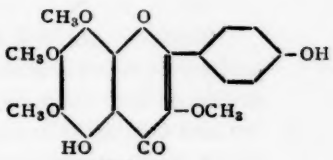
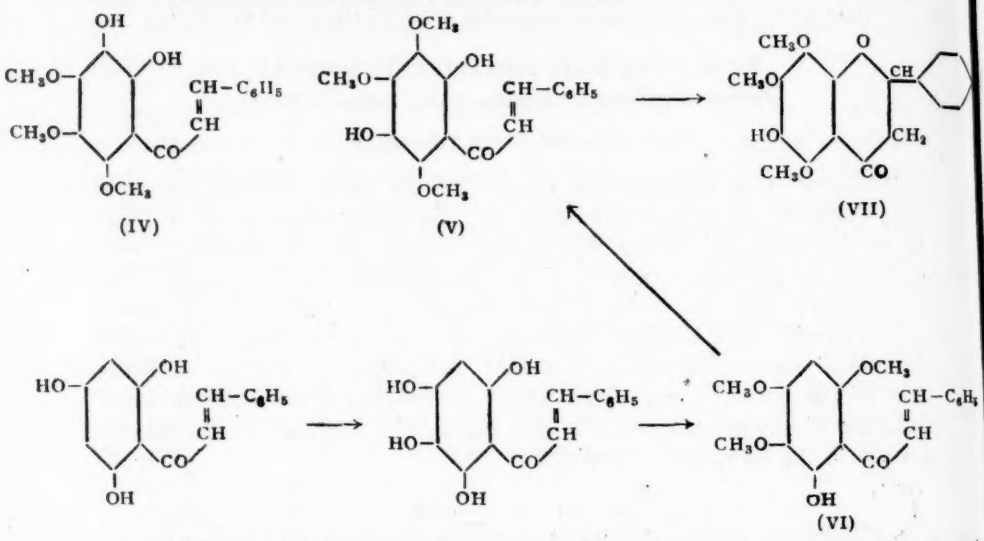


(III)

Among the components of *D. pedicellata*, the chemical constitution of pedicellin has been definitely established by degradation studies[3] and also by synthesis.[4] Though pedicin and pedicinin are closely related to it and the conversion of pedicin into pedicellin on the one hand and into pedicinin on the other and the preparation of pedicinin from pedicellin have been carried out, the exact constitutions of these two do not appear to have been conclusively established.

Pedicin was given the constitution of an ortho-dihydroxy chalkone as in (IV) by Sharma and Siddiqui.[3] As evidence they recorded that it was capable of undergoing methylation to yield pedicellin and ring closure to form an isomeric compound and that it gave colour with ferric chloride and formed a coloured insoluble lead salt. The conclusion that it was an ortho-dihydroxy compound did not appear to us to be well supported. A para

dihydroxy structure as in formula (V) seemed to be more probable and this was in accordance with the considerations of biogenesis based on the general theory of Robinson[5] in which the stages in the oxidation of the phloroglucinol part may be expected to be as given below:



Siddiqui[1] recorded that pedicin gave with ferric chloride an evanescent greenish blue colouration quickly changing to pale yellow which then slowly developed into deep red and later reddish brown. We have repeated this test and confirm it except for the small difference that the initial evanescent colour is an opaque brown and not greenish blue. On the whole the behaviour of the substance with ferric chloride is characteristic of a quinol ketone and not of a catechol derivative which could be expected to give a stable green. On treatment with lead acetate the solution remains clear for about two hours and only afterwards a brown precipitate is slowly formed. This agrees with the reaction of quinol ketones; catechol derivatives on the other hand give precipitates immediately.

The new structure of pedicin is confirmed by its synthesis using the nuclear oxidation of 2-hydroxy-3 : 4 : 6-trimethoxy chalkone (VI) by means of alkaline persulphate. The reaction takes place readily and a good yield of pedicin (V) is obtained. That such oxidation of hydroxy chalkones is feasible has been shown recently by Rajagopalan and Seshadri[6] using simpler examples. The synthetic pedicin undergoes methylation to pedicellin and reacts with bromine to yield pedicinin. The methylation of pedicinin has been studied

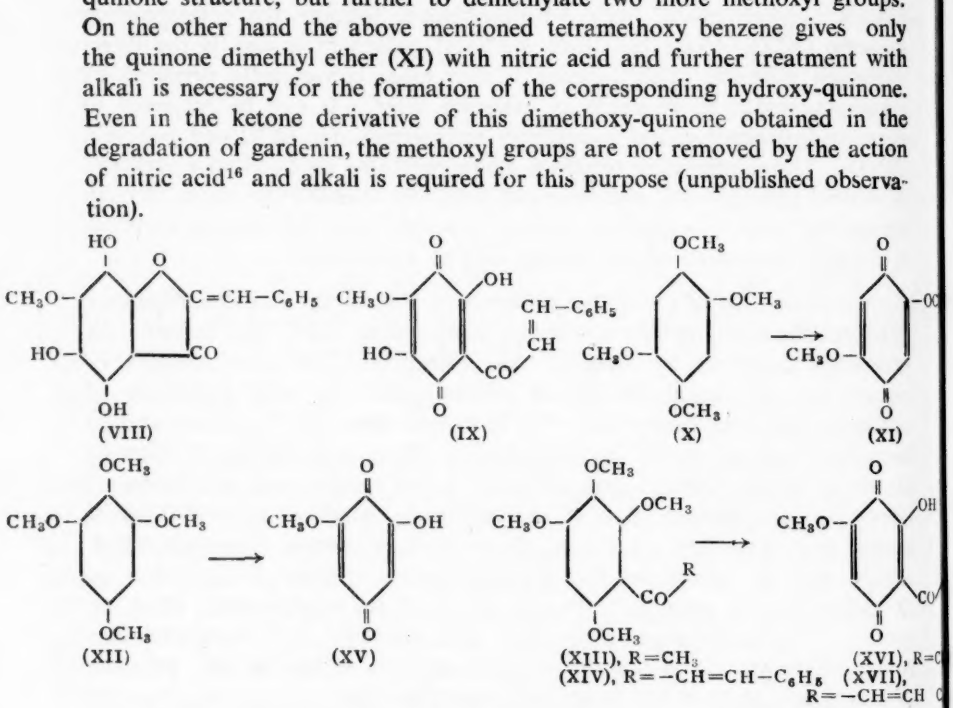
using several methods (Rao, Rao and Seshadri[11]). Methyl iodide or dimethyl sulphate and potassium carbonate did not work satisfactorily; on the other hand, diazomethane effects partial methylation readily yielding methyl pedicinin. Thus these experiments constitute a new total synthesis of all the four compounds.

Just as the quinol derivatives of flavones, pedicin also undergoes ready oxidation when treated with *p*-benzoquinone, forming the corresponding quinone (XIX). This has three methoxyl groups in it and is the direct oxidation product. This quinone is also more conveniently prepared by employing moist silver oxide as oxidising agent. It can be subjected to stepwise hydrolysis giving successively methyl pedicinin (XX) and pedicinin (XXI). These interesting reactions again constitute an alternative synthesis of methyl pedicinin and pedicinin and definitely establish the stages through which the pedicin—pedicinin change proceeds with the help of bromine. A detailed discussion of this change will be made later.

In the course of the above synthesis of pedicin the isomeric flavanone (VII) could also be readily obtained. It melted at 105–7° and had all the properties described by Siddiqui[1] for isopedicin. The transformation of pedicin into this substance can be effected under the usual conditions of chalkone-flavanone conversion. We have not been able to obtain pseudo isopedicin melting at 125° as described by Warsi and Siddiqui.[7] Viewing all these results together and particularly the spontaneous conversion of isopedicin into pseudo-isopedicin as reported by the above authors[7] it would appear that these two are forms of the same substance, isopedicin which should now be given the 6-hydroxy-flavanone structure (VII). Thus in *D. pedicellata* we meet with the occurrence of the related pair, chalkone (pedicin, V) and flavanone (isopedicin, VII) together. Such a combination is not unknown; as a relevant example may be mentioned the presence of butein and butin in the flowers of *Butea frondosa*.[8]

A knowledge of the correct structure for pedicin is of importance in arriving at the constitutions of methyl pedicinin and pedicinin which accompany it in the leaves. Pedicinin was first given the benzylidine coumaranone formula (VIII) by Sharma and Siddiqui.[3] Subsequently Bose and Dutt[9] showed that it had the characteristic properties of a quinone and hence should be given the quinone-chalkone constitution (IX), thus supporting the earlier suggestion of Price and Robinson[10] that the pedicin group might have some resemblance to dunnione since the plant sources, Streptocarpus and Didymocarpus are closely related botanically. They[9] explained the conversion of pedicellin (I) into pedicinin as due to combined oxidation and

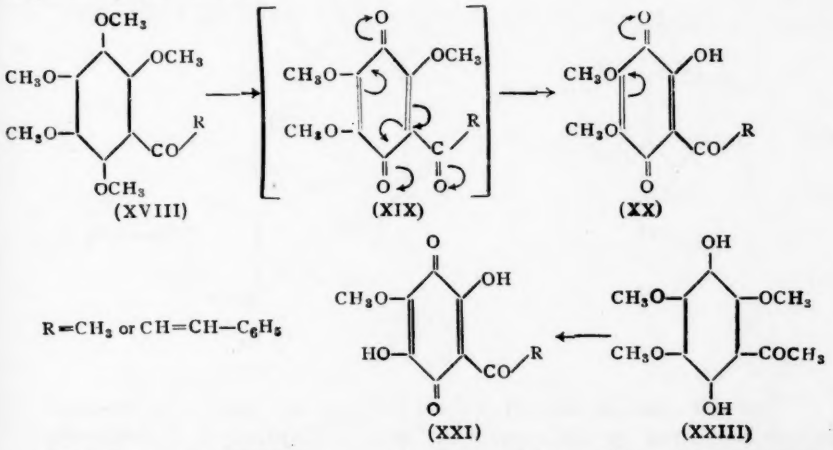
demethylation with nitric acid and showed that the unsaturation in the side chain plays no part in this change. In support of this they quoted the only analogy available at that time of the conversion of 1:2:4:5-tetramethoxy benzene (X) into the dimethoxy-quinone (XI). It might be said that this analogy was not adequate. Actually, as they themselves showed, the treatment of pedicellin with nitric acid alone is enough not only to form the quinone structure, but further to demethylate two more methoxyl groups. On the other hand the above mentioned tetramethoxy benzene gives only the quinone dimethyl ether (XI) with nitric acid and further treatment with alkali is necessary for the formation of the corresponding hydroxy-quinone. Even in the ketone derivative of this dimethoxy-quinone obtained in the degradation of gardenin, the methoxyl groups are not removed by the action of nitric acid[16] and alkali is required for this purpose (unpublished observation).



However, the correctness of their interpretation is amply supported by the recent publication of Rao, Rao and Seshadri[11] on oxidative demethylation with nitric acid employing a variety of compounds, some of which are closely analogous to pedicellin. It has been shown by them that a number of these and particularly 1:2:4:5-tetramethoxy benzene and its derivatives yield only methoxy quinones. On the other hand, 1:2:3:5-tetramethoxy benzene (XII) and its derivatives, ketones (XIII) or chalkones (XIV), invariably yield directly hydroxy quinones due to the combined effect of oxidative demethylation to form the quinone structure along with further demethylation of suitably located methoxyl groups. It should be noted

that only one of the methoxyl groups of the 2:6-dimethoxy quinone undergoes hydrolysis. The other methoxyl is stable and cannot be hydrolysed even with alkali. This stability to alkali has now been definitely proved using as examples the ketone (XVI) and chalkone (XVII). They are recovered unchanged from their solutions in aqueous alkali. The hydroxy-methoxy quinone (XV) itself is unsuitable for this test since it undergoes rapid polymerisation in alkali. The above partial demethylation could be understood from the fact that a quinone carbonyl is capable of activating only one methoxyl group present in the β-position of the katioenoid system. In the case of the ketones (XVI) and chalkones (XVII) the particular methoxyl group involved in this second stage demethylation is also ortho to the ketonic carbonyl. The orientation of the hydroxyl and methoxyl groups given in formulæ (XVI and XVII) has already been proved in the earlier paper[11] not only from the reactions of the compounds but also by their preparation in different ways leaving no doubt about their structure.

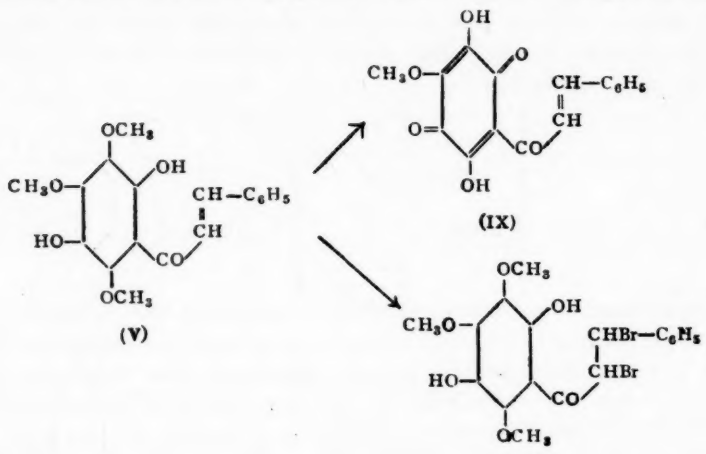
It is significant that the side chain unsaturation is unnecessary for the changes discussed above, since the simpler tetramethoxy benzene and ketones undergo the reaction readily. Additional evidence is given in the present paper by the oxidative demethylation of 2:3:4:5:6-penta-methoxy-aceto-phenone (XVIII, $R = CH_3$) which behaves quite analogous to pedicellin (I) and forms a dihydroxy-quinone (XXI, $R = CH_3$) similar to pedicinin (IX). The reaction in both cases could be represented as taking place in stages as given below:



The first stage (XIX) has not been isolated in this reaction but has been obtained from pedicin. The second stage is represented by methyl

pedicinin (XX, R = — CH = CH — C_6H_5). In this change the methoxyl in the 2-position is more easily hydrolysed since, as already explained, it is subjected to the influence of two katioenoid systems whereas that in the 5-position is affected by only one. The methoxyl in position 4- is left out for reasons already given.

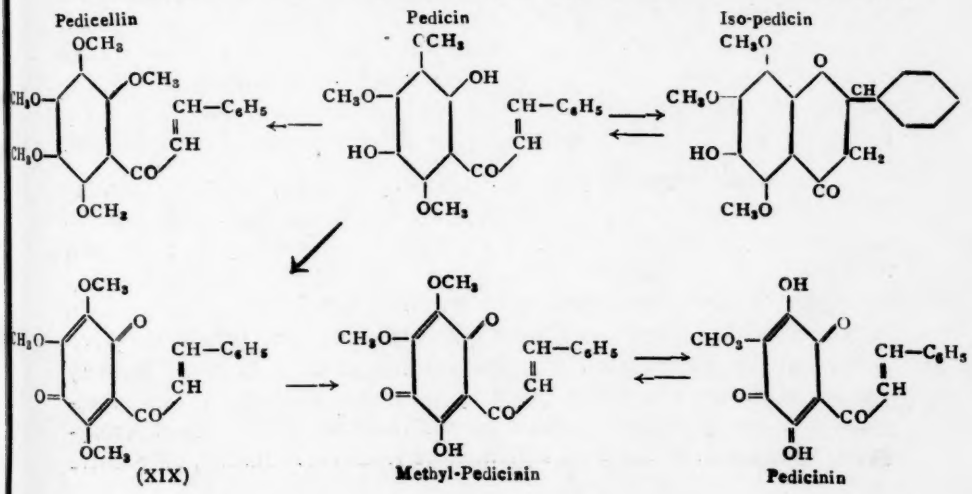
As pointed out by Salooja, Sharma and Siddiqui, Bose and Dutt did not explain the pedicin-pedicinin change by means of bromine and we may add, the permanganate oxidation to pedicinin. There was definite difficulty at that time because the constitution adopted for pedicin was wrong. No such difficulty exists with the new correct constitution (V) now presented. The reaction is a simple dehydrogenation of a quinol to quinone with the hydrolysis of the susceptible methoxyl groups by the hydrogen bromide formed. That this is so is definitely proved by the dehydrogenation of pedicin using benzoquinone or silver oxide to the quinone (XIX) which subsequently undergoes stepwise demethylation and in these changes the extranuclear double bond is evidently unaffected. The quantitative studies of Salooja, *et al.*, using one molecular proportion of bromine would indicate that there are two simultaneous reactions, one involving the quinol grouping and leading to the formation of pedicinin (IX) and the other involving the side chain double bond and leading to the formation of dibromo-pedicin (XXII).



That side chain unsaturation does not play any part in the oxidation is further supported by our experiment on 2 : 5-dihydroxy-3 : 4 : 6-trimethoxy-acetophenone (XXIII) using bromine whereby the hydroxy-quinone-ketone (XXI, R = CH_3) is readily obtained.

That the conversion of a quinol into quinone involves a dehydrogenation is well established. A number of dehydrogenating agents could be used. The successful use of bromine for this purpose would depend on the possibility of other simultaneous reactions that can be promoted by bromine. One of the earliest dehydrogenations of this type was mentioned by Perkin[17] in connection with the study of excœcarin. This compound which was isolated from green ebony (*Excœcaria jacarandi*) when treated with bromine was converted into the corresponding quinone excœcarone which could be reduced to the original compound by sulphurous acid. As a further example, the action of bromine on 2:6-dimethoxy quinol has been studied now. This yields 2:6-dimethoxy-3:5-dibromo-quinone by dehydrogenation and bromination. With pedicin, bromine effects demethylation besides dehydrogenation. In this reaction the successful production of pedicinin would appear to depend upon the rather poor ethylenic reactivity of chalkones; as a side reaction the addition of bromine to pedicin will not be helpful for the formation of pedicinin.

The new total synthesis of pedicin and its derivatives recorded in this paper has a strong biogenetic significance. The occurrence of methyl pedicinin in the leaves of *D. pedicellata* along with the other four has been established. Pedicin would appear to be the primary compound of this group and it occurs as a major component. The stages of its evolution from the simplest phloroglucinol derivative have already been indicated. The first stage, *i.e.*, the formation of the tetrahydroxy chalkone is supported by the persulphate oxidation of 2-hydroxy-4:6-dimethoxy chalkone reported



in an earlier publication.[6] The plant should be using some protective mechanism other than methylation. The second stage (VI to V) leading to the synthesis of pedicin has been described in this paper. The later transformations can be represented as given above:

In the experiments described in this paper each of these stages has been obtained. The simple oxidation of pedicin has to be carried out with *p*-benzoquinone or better with silver oxide and the subsequent hydrolysis can be effected in stages. Bromine as a reagent is unsuited for these graded transformations. From the plant source, though methyl pedicinin could be isolated by careful extraction, the simple quinone (XIX) has not so far been isolated.

It is appropriate here to emphasise the close relationship between methyl pedicinin and pedicinin. They are mutually inter-convertible. Sharma and Siddiqui effected the conversion of methyl pedicinin into pedicinin by the action of dilute alkali. From the experiments of Bose and Dutt it is clear that this change could be brought about by nitric acid itself. As a result of experiments on methylation it has now been shown that the reverse change of pedicinin to methyl pedicinin can be effected very satisfactorily by means of diazomethane. Since it is known that in plants methylation and demethylation mechanisms exist, it may be more correct to say that methyl pedicinin can not only be formed as a stage in the conversion of pedicin to pedicinin, but also that it is capable of being produced independently by the methylation of pedicinin. In this connection another point should also be mentioned. Though pedicinin contains two hydroxyl groups as pointed above, only one of these undergoes methylation with diazomethane; the other is resistant just as in the case of ortho-hydroxy carbonyl compounds. This is in agreement with the suggestion made earlier,[11] that though the compound is quinonoid the conditions necessary for chelation exist and ortho-hydroxy-quino ketones are chelated compounds.

Contradictory reports have been made by previous workers regarding certain reactions of pedicinin and methyl pedicinin and have been used to support different points of view. As a typical example may be mentioned the colour reaction with ferric chloride. Siddiqui, *et al.*, reported that they give a red colour whereas Bose and Dutt failed to observe this colour. In agreement with the former authors we find that they give definite deep red colour but this positive colour reaction is not at all against the hydroxy quinone chalkone constitution given by the other authors for these compounds. Actually this is a characteristic reaction of all the hydroxy-quinone-ketones and chalkones that we have examined. Indeed, all positive

experimental results so far recorded, for example their marked acidic property, could be satisfactorily explained only on the basis of these structures and other alternative formulations seem to be unnecessary and to lack support from chemical possibilities and analogies. For properly understanding some of the other observations it may be useful to emphasise here that quinones do differ in their reducibility and that the side chain double bond of chalkones has somewhat diminished ethylenic reactivity owing to conjugation with the neighbouring carbonyl forming part of the well-known katioenoid system.[13]

Experimental

Extraction of the leaves: (Isolation of methyl pedicinin and other compounds)

Air-dried leaves of *Didymocarpus pedicellata* were extracted with ether and the ether extract concentrated to small bulk. On allowing it to stand for a few days an orange red crystalline solid separated out which was filtered and washed with a little ether. When crystallised from ethyl acetate it appeared as orange red elongated rectangular prisms melting at 143–45° thus agreeing with the melting point reported for pedicin. The identity was confirmed by the preparation of the colourless dibenzoate melting at 181–83°.

The original ethereal filtrate was diluted with a large excess of ether (to prevent the formation of emulsions) and shaken with 5% aqueous sodium bicarbonate twice. The ether layer was separated out and marked (A). The dark reddish brown bicarbonate extract was acidified with concentrated hydrochloric acid and extracted with ether. On concentrating this ether solution an orange red solid crystallised out. It was filtered and washed with a mixture of ether and light petroleum. When crystallised from a mixture of benzene and ligroin the first crop consisted of dark red flat needles melting at 203–5° and this was identified as pedicinin. The mother-liquor on concentration yielded an orange yellow solid which when recrystallised from the same solvent came out as orange yellow short prismatic needles melting at 110–12° and agreed in all its properties with methyl pedicinin. (Found: C, 64·6; H, 4·2; $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%.) For the above identifications authentic samples obtained from pedicellin by the method of Sharma and Siddiqui were used for direct comparison. The yield of methyl pedicinin was 0·5%.

Methyl pedicinin (0·5 g.) thus obtained was dissolved in 5% aqueous sodium hydroxide and the solution treated with solid sodium hydroxide whereby a red solid crystallised out. This sodium salt was rapidly filtered,

dissolved in water (10 c.c.) and the solution acidified. The orange coloured precipitate was filtered, washed with water and crystallised from chloroform. It formed deep red needles melting at 203–5° identical with pedicinin.

The ether solution (A) left after extraction with bicarbonate was then shaken with 5% aqueous sodium hydroxide twice and then with dilute acid. Acidification of the alkaline extract with hydrochloric acid and extraction with ether gave some more of pedicin. The residual pale greenish ether solution was concentrated to small bulk and treated with light petroleum whereby pedicellin crystallised out.

Pedicin

The sample of pedicin was purified by crystallisation from ethyl acetate when it came out as dark red big prisms. From benzene it separated as orange red elongated rectangular plates melting at 143–45°. In aqueous sodium hydroxide it readily dissolved to a reddish violet solution. In alcoholic solution it gave an opaque brown colour with a drop of ferric chloride solution. This very rapidly faded away to pale yellowish brown. Further small additions of the reagent led to a repetition of the colour changes till eventually the solution assumed a permanent reddish brown. It did not give any immediate precipitate with alcoholic lead acetate but on keeping for two hours a brown precipitate slowly formed.

Pedicin is considerably toxic to fish which show definite toxic symptoms (turning upside down) in 2·5 minutes for a concentration of 150 mg. per litre, and in 3·5 minutes for a concentration of 100 mg. per litre. But its easy oxidisability makes it feebly toxic at lower concentrations (*e.g.*, 50 mg. per litre) since, before the toxic effect could be exerted the compound seems to undergo change. As a possible oxidation product pedicinin has also been tested and is found to have no appreciable toxicity in a concentration of 150 mg. per litre.

Conversion of pedicin into isopedicin

A solution of pedicin (0·5 g.) in alcohol (20 c.c.) and water (10 c.c.) was treated with concentrated hydrochloric acid (2 c.c.). The mixture was refluxed on a water-bath for 24 hours. The alcohol was removed under reduced pressure, the residue treated with water (50 c.c.) and extracted with ether. The ether extract was dried over anhydrous sodium sulphate and distilled. The orange red liquid residue left behind, on the addition of a little ether yielded an almost colourless crystalline solid. It was treated with a mixture of ether and light petroleum (1 : 1) and the solid filtered. When recrystallised from a mixture of benzene and light petrol the product

appeared as almost colourless prismatic needles melting at 105–7°. Further crystallisation did not improve the melting point. It was easily soluble in alcohol and the alcoholic solution did not give any appreciable colour immediately with ferric chloride but a pale brown colour appeared slowly. Yield 0·4 g. In aqueous sodium hydroxide it readily dissolved to a bright yellow solution which quickly changed to reddish violet and on acidification this yielded pedicin.

2-*Hydroxy*-3 : 4 : 6-*trimethoxy-chalkone* (*VI*)

A solution of 2-hydroxy-3 : 4 : 6-trimethoxy acetophenone[4, 14] (3 g.) in alcohol (25 c.c.) was treated with benzaldehyde (10 c.c.) and aqueous potash (25 g. in 20 c.c. of water). Sufficient alcohol was added to get a homogeneous solution which was kept tightly stoppered for 3 days. It was then poured into water (800 c.c.) and the solution extracted twice with ether. The clear orange red alkaline solution was acidified whereby a red liquid product separated which readily crystallised. It was filtered, washed with aqueous sodium bicarbonate followed by water and crystallised from alcohol. It came out as orange red needles melting at 140–42°. (Found: C, 69·0; H, 5·9; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%.) Yield 4 g. It was sparingly soluble in aqueous sodium hydroxide and gave a reddish brown colour with ferric chloride in alcoholic solution.

2 : 5-*Dihydroxy*-3 : 4 : 6-*trimethoxy chalkone* (*Pedicin*) (*V*)

To a stirred solution of 2-hydroxy-3 : 4 : 6-trimethoxy chalkone (VI) (2·5 g.) in a mixture of pyridine (15 c.c.) and aqueous potash (3 g. in 30 c.c.) was added potassium persulphate solution (3 g. in 100 c.c.) gradually with cooling to 10–15° during the course of 2 hours. The dark brown solution was allowed to stand for 24 hours, acidified with concentrated hydrochloric acid and the unchanged chalkone removed by extracting twice with ether. Th clear brown aqueous solution was treated with sodium sulphite (2 g.), concentrated hydrochloric acid (30 c.c.) and benzene (100 c.c.) and refluxed for 30 minutes. The benzene layer was separated and the aqueous layer extracted once more with a little benzene. The total benzene extract was dried over sodium sulphate and distilled when a red liquid was left behind which quickly crystallised. It was purified by recrystallisation from benzene when it separated out in the form of bright orange red elongated rectangular plates melting at 143–45°. Mixed melting point with an authentic sample of natural pedicin was not depressed. (Found: C, 65·2; H, 5·2; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%.) Yield 0·5 g. Its solubility and colour reactions were identical with those given by the natural sample.

Benzoylation

The above dihydroxy chalkone (0·1 g.) was dissolved in pyridine (3 c.c.) and treated with benzoyl chloride (0·2 c.c.). The orange coloured solution was kept for one hour and poured into dilute hydrochloric acid. The white solid obtained after keeping for 3–4 hours was filtered, ground well with very dilute sodium hydroxide followed by water. Crystallisation from a mixture of benzene and ligroin yielded colourless narrow rectangular plates melting at 181–83°. A mixture of this and dibenzoyl pedicin prepared from the natural sample according to the method of Sharma and Siddiqui also melted at 181–83°.

Methylation

The above dihydroxy chalkone (0·1 g.) on being heated for 6 hours with dimethyl sulphate (0·2 g.) and potassium carbonate (1 g.) in anhydrous acetone solution yielded a colourless crystalline methyl ether melting at 97–98° identical with pedicellin.

Methylation of Pedicinin to Methyl Pedicinin

A clear solution of pedicinin (0·5) g. in absolute alcohol (50 c.c.) was treated with an ethereal solution of diazomethane prepared from nitroso-methyl urea (1·5 g.). The mixture was kept for 48 hours in the ice-chest with a stopper carrying a capillary tube serving as an outlet for the escaping gases. The solvents were then distilled off, and the residue extracted with ether. On concentrating the ether extract an orange coloured solid was slowly deposited. It was filtered, washed with a little ether and recrystallised from a mixture of benzene and ligroin. It appeared as orange coloured rectangular prisms melting at 110–12° alone or in admixture with the sample of methyl pedicinin prepared from pedicellin.

Dehydrogenation of Pedicin to 2 : 4 : 5-*trimethoxy*-3 : 6-*quino-chalkone*

First Method.—A solution of pedicin (0·2 g.) in ether (20 c.c.) was treated with *p*-benzoquinone (0·2 g.). The bright orange colour of the solution did not appreciably change. After keeping for 30 minutes, the solvent was distilled off and the greenish yellow solid left behind was extracted with boiling ligroin. The solution was filtered from the greenish black crystals of quinhydrone also formed in the reaction. The filtrate deposited on cooling bright golden yellow rectangular plates of the trimethoxy-quino-chalkone which was filtered and washed with a little ether. It melted at 113–14°. (Found: C, 65·7; H, 5·1; OCH_3, 27·9; $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9; for 3 OCH_3 28·4%.) It was sparingly soluble in ether and ligroin and in alcoholic solution it did not give any colour with ferric

chloride. It was not soluble in aqueous sodium bicarbonate but on keeping in contact with the solution it dissolved very slowly in the course of a few hours. In aqueous sodium hydroxide it dissolved within 2 minutes forming a deep red solution. Yield, 0·1 g.

It is necessary to note that the quinone corresponding to pedicin is only yellow as compared with the deep orange red pedicin. Consequently in the gossypetone test (treatment with *p*-benzoquinone) there is no intensification in colour in the case of pedicin though it readily undergoes oxidation.

Second Method.—Pedicin (0·35 g.), dissolved in ether (40 c.c.) was shaken vigorously with moist silver oxide (about 0·5 g., freshly prepared and thoroughly washed) for about 15 minutes. It was then stirred well with anhydrous sodium sulphate (5 g.) and filtered. On evaporating the filtrate the quinone separated out as bright golden yellow thin rectangular plates melting at 113–14°. The mixed melting point with the quinone prepared using *p*-benzoquinone was not depressed. Its properties were also identical. Yield, 0·32 g.

Reduction of the Trimethoxy-quino-chalkone to Pedicin

The trimethoxy-quino-chalkone (50 mg.) prepared by the above methods was dissolved in glacial acetic acid (3 c.c.) and treated with sodium sulphite (0·5 g.). The solution was heated for a minute and kept at the room temperature for 15 minutes. Water (50 c.c.) was added and the orange coloured crystalline solid filtered and washed with water. It melted at 143–45° and was identical with pedicin.

Hydrolysis of the trimethoxy-quino-chalkone

(*a*) *To Methyl Pedicinin.*—The trimethoxy-quino-chalkone (50 mg.) was dissolved in alcohol (5 c.c.) and the solution treated with 5% aqueous sodium bicarbonate (10 c.c.). After mixing thoroughly, water (50 c.c.) was added, the mixture filtered and the clear red filtrate acidified with dilute hydrochloric acid. After keeping for 30 minutes the orange coloured fine woolly needles that separated out were filtered and washed with water. They melted at 110–12° alone or in admixture with methyl pedicinin. This sample of methyl pedicinin could be hydrolysed to pedicinin by the already known methods used in the past.

(*b*) *To Pedicinin.*—When the trimethoxy-quino-chalkone (50 mg.) was treated with 5% aqueous sodium hydroxide (10 c.c.) it gradually dissolved in two minutes. The deep red solution, when acidified, yielded an orange coloured solid which crystallised from chloroform as deep red flat needles

melting at 202–03° and identical with pedicinin. This hydrolysis could be effected even by treating the alcoholic solution with concentrated hydrochloric acid (1 c.c.) and diluting it with water after a minute.

Iso-Pedicin VII

2-Hydroxy-3 : 4 : 6-trimethoxy-chalkone (VI) (1 g.) was oxidised with alkaline potassium persulphate as described earlier, but the product was worked up in a different manner in which the effect of acid was prolonged. After removing the unchanged chalkone by extracting with ether the aqueous solution was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and kept in a boiling water-bath for 30 minutes. After cooling, the solution was extracted with ether and the ether distilled off whereby an orange red liquid product was obtained which after keeping for one week at the ordinary temperature became a very pale brown crystalline solid. Recrystallisation of this from a mixture of ether and light petroleum yielded almost colourless rectangular plates melting at 105–7°. It agreed in all its properties with the sample of isopedicin prepared from pedicin as described earlier and the mixed melting point was not depressed. (Found: C, 65·1; H, 5·2; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%.)

Action of bromine on 2 : 6-*dimethoxy-quinol*

A solution of 2 : 6-dimethoxy-quinol (0·5 g.) in chloroform (30 c.c.) was treated with a solution of bromine in the same solvent till there was a slight excess. After keeping for 15 minutes the solvent was evaporated in a basin and the red crystalline solid was recrystallised from chloroform. It formed bright red plates melting at 175–76° and was identical with 2 : 6-dimethoxy-3 : 5-dibromobenzoquinone made from 2 : 6-dimethoxy quinone by the method of Robinson and Vasey.[15] When exactly one molecular proportion of bromine was added the product was not homogeneous and the mixture could not be separated.

Action of bromine on 2 : 5-*dihydroxy*-3 : 4 : 6-*trimethoxy acetophenone*[4] (XXIII)

To a solution of the ketone (1 g.) in chloroform (10 c.c.) was added a solution of bromine in chloroform (7 c.c. containing 0·7 g. of bromine) and the reaction mixture allowed to stand for 2 hours. There was copious evolution of hydrogen bromide throughout the course of the reaction. The chloroform was then removed under reduced pressure and the residue treated with water (10 c.c.). The mixture was extracted with ether twice and the ether extract dried over sodium sulphate and evaporated. The dihydroxy-quinone-ketone was obtained as a dark red oil which solidified on the addition of a few drops of ether. It was filtered, washed with ether

and recrystallised from benzene when it separated out as dark red needles melting at 165–67°. (Found: C, 51·0; H, 3·9; $C_9H_8O_6$ requires C, 50·9; H, 3·5%.) Yield, 0·25 g. It was readily soluble in aqueous sodium bicarbonate with effervescence giving a red solution. With aqueous sodium hydroxide it gave a dark red solution. In alcoholic solution it produced a red colour with ferric chloride. It was sparingly soluble in ether and benzene but more easily soluble in chloroform. It was identical with the sample obtained by the action of nitric acid on pentamethoxy-acetophenone.

2:3:4:5:6-*Pentamethoxy acetophenone*[4] (*XVIII*, $R = CH_3$).

The above is more conveniently prepared as follows: A solution of 2:5-dihydroxy-3:4:6-trimethoxy-acetophenone (1·5 g.) in anhydrous acetone (25 c.c.) was refluxed with dimethyl sulphate (2 c.c.) and potassium carbonate (5 g.) for 8 hours. The solvent was then removed under reduced pressure and the residue treated with water. Extraction with ether, drying the ether extract with calcium chloride and evaporation gave a pale yellow liquid which on keeping for some time yielded an almost colourless crystalline solid melting at 43°. Yield 1 g.

Oxidative demethylation of the pentamethoxy acetophenone

The above pentamethoxy acetophenone (1 g.) was dissolved in anhydrous ether (10 c.c.) and the clear pale yellow solution cautiously treated with fuming nitric acid (d. 1·5, 1 c.c.). After keeping the bright red reaction mixture for 3 hours, water (20 c.c.) was added and thoroughly shaken. The ether layer was separated, the aqueous layer extracted twice with ether, the combined ether extract dried over anhydrous sodium sulphate and evaporated. The red liquid left behind crystallised on standing for some time at the ordinary temperature. The red crystalline solid was filtered, washed with ether and recrystallised from benzene when it formed red needles melting at 165–67° alone or in admixture with the sample of the quinone obtained from 2:5-dihydroxy-3:4:6-trimethoxy acetophenone by treatment with bromine. The properties were also identical.

Summary

Pedicin is considered to be a *para*-dihydroxy chalkone and this constitution is confirmed by its synthesis from 2-hydroxy-3:4:6-trimethoxy chalkone using the method of nuclear oxidation with persulphate. The synthetic pedicin could be readily converted into pedicellin and pedicinin. Under the ordinary conditions of chalkone-flavanone conversion it yields isopedicin which is therefore given the constitution of 6-hydroxy-5:7:8-trimethoxy flavanone. The constitutions of pedicinin and methyl pedicinin

are discussed on the basis of the analogies presented in an earlier paper on oxidative demethylation using nitric acid and fresh data derived from the conversion of 2:5-dihydroxy-3:4:6-trimethoxy acetophenone and pentamethoxy acetophenone into hydroxy-quinone-ketone analogous to pedicinin. It is concluded that pedicinin and methyl pedicinin have the hydroxy-quinone-chalkone structure. Methyl pedicinin which is an intermediate stage in the formation of pedicinin is now found to occur in the leaves of *D. pedicellata*. A scheme of biogenesis of pedicin and its allies is given. The most conclusive evidence for this scheme as well as for the mechanism of the pedicin-pedicinin change and incidentally for the pedicellin-pedicinin change also, is the gentle oxidation of pedicin to the trimethoxy-quino-chalkone and further stepwise hydrolysis to methyl pedicinin and pedicinin. Using diazomethane for partial methylation it is possible to methylate pedicinin to methyl pedicinin.

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